U.S. DEPARTMENT OF COMMERCE
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PB-259 930

Treatment of Acid Mine Drainage by the Alumina-Lime-Soda Process

Midwest Research Inst, Kansas City, Mo

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio Office of Research and Development

Sep 76

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-206	2.
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: Treatment of Acid Mine Drainage by the Alumina-Lime-Soda Process	5. REPORT DATE: September 1976 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): J. W. Nebgen, D. F. Weatherman, M. Valentine, and E. P. Shea	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Midwest Research Institute, Kansas City, Missouri 64110	10. PROGRAM ELEMENT NO. 1BB610
	11. CONTRACT/GRANT NO. S-802816
12. SPONSORING AGENCY NAME AND ADDRESS: Industrial Environmental Research Laboratory, Office of Research and Development, U. S. Environmental Protection Agency, Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED: Final 8/74 - 12/75
	14. SPONSORING AGENCY CODE: EPA-ORD
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

The alumina-lime-soda process is a chemical desalination process for waters in which the principal sources of salinity are sulfate salts and has been field tested at the Commonwealth of Pennsylvania's Acid Mine Drainage Research Facility, Hollywood, Pennsylvania, as a method to recover potable water from acid mine drainage. The alumina-lime-soda process involves two treatment stages. Raw water is reacted with sodium aluminate and lime in the first stage to precipitate dissolved sulfate as calcium sulfoaluminate. In the second stage, the alkaline water (pH = 12.0) recovered from the first stage is carbonated to precipitate excess hardness. Following carboration, product water meets USPHS specifications for drinking water.

Alumina-lime-soda process economics are influenced most by the cost of sodium aluminate. Widespread application of the alumina-lime-soda process will increase demand for sodium aluminate, and should spur interest in alternate sources of this treatment chemical.

Operating costs for recovering potable water from an acid mine drainage having an acidity of 700 mg/liter and a sulfate level of 750 mg/liter are estimated to be in the range of $0.21 to $0.27/m³ ($0.79 to $1.04 per 1,000 gal).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Calcium hydroxides Neutralizing *Drainage - mine (excavations) Cost comparison pH control Aluminum oxide Demineralizing	Acid Mine Drainage Coal Mine Drainage Ferric iron Pennsylvania Ferrous iron Softening - mine drainage	13B 08/G 08/H

18. DISTRIBUTION STATEMENT: Release to public	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 105
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: 5.50

EPA Form 2220-1 (9-73)

*USGPO: 1976 — 757-695/6111 Region 5-11

327130

PB 259 930

EPA-600/2-76-206
September 1976

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EPA-600/2-76-206
September 1976

TREATMENT OF ACID MINE DRAINAGE BY THE ALUMINA-LIME-SODA PROCESS

by

J. W. Nebgen, D. F. Weatherman, M. Valentine, and E. P. Shea

Midwest Research Institute
Kansas City, Missouri 64110

Grant No. S-802816

Project Officer

Roger C. Wilmoth
Resource Extraction and Handling Division
Crown Mine Drainage Control Field Site
Rivesville, West Virginia 26588

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report describes the adaptation of a treatment process, originally developed for desalination of brackish water, for use in producing a high-quality effluent from acid mine drainage. The process involves lime addition to pH 12 combined with sodium aluminate addition to precipitate calcium and sulfate as calcium sulfoaluminate rather than calcium sulfate. In this manner, the sulfate levels can be drastically reduced and the effluent from the process can, in most cases, meet chemical and microbiological standards for potable water. The process provides an option heretofore not available with neutralization processes treating acid mine drainage--namely, the production of a product water meeting chemical and microbiological standards for potability. This is one of several projects undertaken by IERL-Ci to develop and demonstrate acid mine drainage treatment and abatement processes to provide alternatives in the selection of treatment facilities to meet the demands of the expanding extractive industries.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

The alumina-lime-soda process is a chemical desalination process for waters in which the principal sources of salinity are sulfate salts and has been field tested at the Commonwealth of Pennsylvania's Acid Mine Drainage Research Facility, Hollywood, Pennsylvania, as a method to recover potable water from acid mine drainage. The alumina-lime-soda process involves two treatment stages. Raw water is reacted with sodium aluminate and lime in the first stage to precipitate dissolved sulfate as calcium sulfoaluminate. In the second stage, the alkaline water (pH = 12.0) recovered from the first stage is carbonated to precipitate excess hardness. Following carbonation, product water meets USPHS specifications for drinking water.

The alumina-lime-soda process is attractive when compared to other water recovery processes, e.g., ion exchange or reverse osmosis. Alumina-lime-soda desalting depends strictly upon chemical processes and thus can be operated using conventional equipment and procedures. The constituents removed are contained in easily dewatered solids. There are no waste liquid streams needing treatment or special handling.

Alumina-lime-soda process economics are influenced most by the cost of sodium aluminate. Widespread application of the alumina-lime-soda process will increase demand for sodium aluminate, and should spur interest in alternate sources of this treatment chemical.

Operating costs for recovering potable water from an acid mine drainage having an acidity of 700 mg/liter and a sulfate level of 750 mg/liter are estimated to be in the range of \$0.21 to \$0.27/m^3 (\$0.79 to \$1.04 per 1,000 gal).

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ACKNOWLEDGMENTS

The principal investigator for this project was Dr. John W. Nebgen, Principal Chemist. He was assisted by Douglas F. Weatherman, Assistant Chemist, who served as project leader, responsible for day-to-day operation of the project, and by Evan P. Shea, Senior Chemical Engineer, and Mark Valentine, Associate Chemical Engineer, who were responsible for the engineering analysis. Field personnel at the Hollywood facility were Michael McGregor and Robert Bartley.

The program was conducted in Midwest Research Institute's Physical Sciences Division, Treatment and Control Processes Section, Dr. A. D. McElroy, Head.

SECTION I

INTRODUCTION

The alumina-lime-soda process for removing calcium sulfate hardness from water was conceived at Midwest Research Institute in 1970 and developed under an Office of Saline Water program during 1971 to 1972.[1/] The process involves two stages which are briefly described as follows.

The first step of the alumina-lime-soda process involves treating brackish water with lime and sodium aluminate at a pH of 12.0. The sodium aluminate removes substantial quantities of calcium and magnesium sulfate as insoluble sulfoaluminates under the high pH conditions.

In the second step, effluent from the lime-sodium aluminate treatment, which is highly alkaline, is treated by addition of carbon dioxide to neutralize the excess causticity and to precipitate calcium carbonate. Thus, the process will yield a completely softened water which will meet drinking water standards if salinity is due to sulfates of calcium and magnesium.

Acid mine drainage (AMD) arises from the oxidation of residual pyrite and marcasite (FeS_2) in active and abandoned coal mines. It consists primarily of dilute sulfuric acid and iron sulfates. Aluminum, calcium, and magnesium sulfates are also present due to neutralization and solubilization of soil materials by the acid. The alumina-lime-soda process is well suited for dealing with the several problems which are posed by acid mine drainage. The process provides for neutralization of acid, removal of iron and hardness components, and for desalination to potable water standards. The sole by-product is a sludge which is readily dewatered, and water recoveries in the 95 to 98% range are possible.

The Commonwealth of Pennsylvania Department of Environmental Resources and the U.S. Environmental Protection Agency funded the first phase of a proposed two-phase study to field test the alumina-lime-soda process for recovering water from acid mine drainage. The Phase I program, presented in the report, was conducted at the Commonwealth of Pennsylvania's Mine Drainage Research Facility at Hollywood, Pennsylvania. A bench-scale unit was installed at the facility, and two mine drainages were evaluated with respect to the alumina-lime-soda process. The primary objective of the program was to obtain information necessary to design, build, and operate a 190,000 liter/day (50,000 gal/day) demonstration plant. This objective was met by obtaining operating experience and experimental data which established alumina-lime-soda chemical and mass balances for the acid mine drainage application and identified other operational and design parameters. The program was particularly sensitive to operational problems which might arise with mine drainage, and to cost-sensitive parameters.

This report will discuss in detail the alumina-lime-soda process in the context of recovering potable water from acid mine drainage.

SECTION II

CONCLUSIONS

Important conclusions drawn from study results are listed below.

1. The alumina-lime-soda process is capable of producing potable water from acid mine drainages. The process is best suited for acid mine drainages having sulfate concentrations ranging between 400 and 1,200 mg/liter.

2. The process economics for recovering potable water using alumina-lime-soda hinge upon costs of sodium aluminate. The high purity sodium aluminate currently marketed in the United States is not an essential requirement for the process. A lower grade sodium aluminate could be manufactured by calcining soda ash and bauxite. Such a product would be adequate and would reduce treatment costs by 30 to 40%.

3. The alumina-lime-soda process can be integrated into conventional waterworks operations and operates very much like conventional lime-soda water softening processes. There are no requirements for sophisticated equipment necessary for other processes to recover potable water from acid mine drainage, e.g., ion exchange or reverse osmosis.

4. Not all raw acid mine drainage needs to be treated by alumina-lime-soda to recover a product water meeting potable water standards. The alumina-lime-soda process will remove sulfate to concentrations of 100 mg/liter or less. Hence, effluent from the alumina-lime-soda reactor can be blended with raw acid mine drainage to obtain product water with a sulfate concentration of 250 mg/liter. The blending also reduces the carbon dioxide requirements in the process second stage where pH is dropped to near 7.0.

5. The alkaline conditions (pH ~ 12.0) and residence time (ca. 90 min) for reacting raw acid mine drainage with alumina-lime-soda chemicals, coupled with the fact that the process operates in the presence of air, preclude the need for a separate unit operation to oxidize iron (II) to iron (III). Oxidation of reduced metallic ions to insoluble trivalent oxides is rapid under the alkaline process conditions.

6. Dissolved iron and aluminum in the raw acid mine drainage are effective in removing a significant portion of the dissolved sulfate during alumina-lime-soda treatment. The lime used in the process to maintain pH 12.0 conditions creates a situation where in situ iron and aluminum will precipitate calcium sulfoferrite and sulfoaluminate salts. Thus, the requirements for sodium aluminate to remove sulfate to 250 mg/liter or less are significantly diminished.

7. The calcium sulfoaluminate and sulfoferrite salts, which contain the salts removed by the alumina-lime-soda process, do not pose serious scaling problems to reactors and pipes. The insoluble calcium sulfosalts act as seeds during the reaction. Thus, the precipitates formed during the reaction tend to find deposition sites on the seed rather than on reaction vessel walls or pipe surfaces.

8. The sole by-product of the alumina-lime-soda process is a mixture of solids containing mainly calcium sulfoaluminate, sulfoferrite, and carbonate. The sludges are microcrystalline and readily dewatered to a cake which can be easily handled. The process does not generate waste salt or acid streams such as those encountered in ion exchange or reverse osmosis operations which require special treatment for adequate disposal.

SECTION III

RECOMMENDATIONS

1. A 190 m^3/day (50,000 gal/day) demonstration plant should be constructed in order to obtain the more detailed process information required for development of full-scale plants designed to recover potable water using the alumina-lime-soda process. The demonstration plant should be operated for 1 year to collect the following information:

* Long-term operation data;
* Chemical requirements;
* Operating costs;
* Labor and power costs;
* Capital costs for full-scale plant; and
* Design and operating criteria.

2. Alternate sources of sodium aluminate should be explored in order to reduce chemical costs of the alumina-lime-soda process. Sodium aluminate obtained by calcining bauxite and soda ash should be evaluated using the small pilot unit. The small-scale experiments for evaluating calcined bauxite/soda ash sodium aluminate can be conducted concurrently with the demonstration study.

SECTION IV

DESIGN OF THE ALUMINA-LIME-SODA PROCESS FOR ACID MINE DRAINAGE

A flow diagram for the recovery of potable water from acid mine drainage (AMD) using the alumina-lime-soda process is presented in Figure 1. The process consists of two basic stages: Stage I--Alumina-Lime-Soda Treatment; and Stage II--Ratio Mixing of Raw AMD/Stage I Effluent and Carbonation. Both stages involve the precipitation of solids which are separated from product water by filtration. The final step of the process is a pH adjustment to produce water meeting drinking water specifications.

As can be seen from Figure 1, raw AMD is first split into two streams. The major fraction is treated by alumina-lime-soda in Stage 1, while the minor stream is mixed with Stage I effluent in the second process stage.

The key process step occurs in Stage 1 where the raw AMD is mixed with the treatment chemicals, i.e., sodium aluminate and hydrated lime. The chemical reactions in this first stage will accomplish the following:

* Neutralize acid;
* Precipitate heavy metals and magnesium; and
* Remove calcium sulfate.

The first two effects are those normally encountered using lime treatment of acid mine drainage; the third effect is unique to the alumina-lime-soda process.

Calcium sulfate is removed during treatment with sodium aluminate and lime because insoluble calcium sulfoaluminates are formed. Calcium sulfate produced by the neutralization of acid and precipitation of heavy metals and magnesium will react at a pH of 12.0 with aluminate ion (from sodium aluminate and <u>in situ</u> aluminum in the mine drainage) to yield mixtures of calcium sulfoaluminates having compositions of $CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot xH_2O$ and $3CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot xH_2O$.

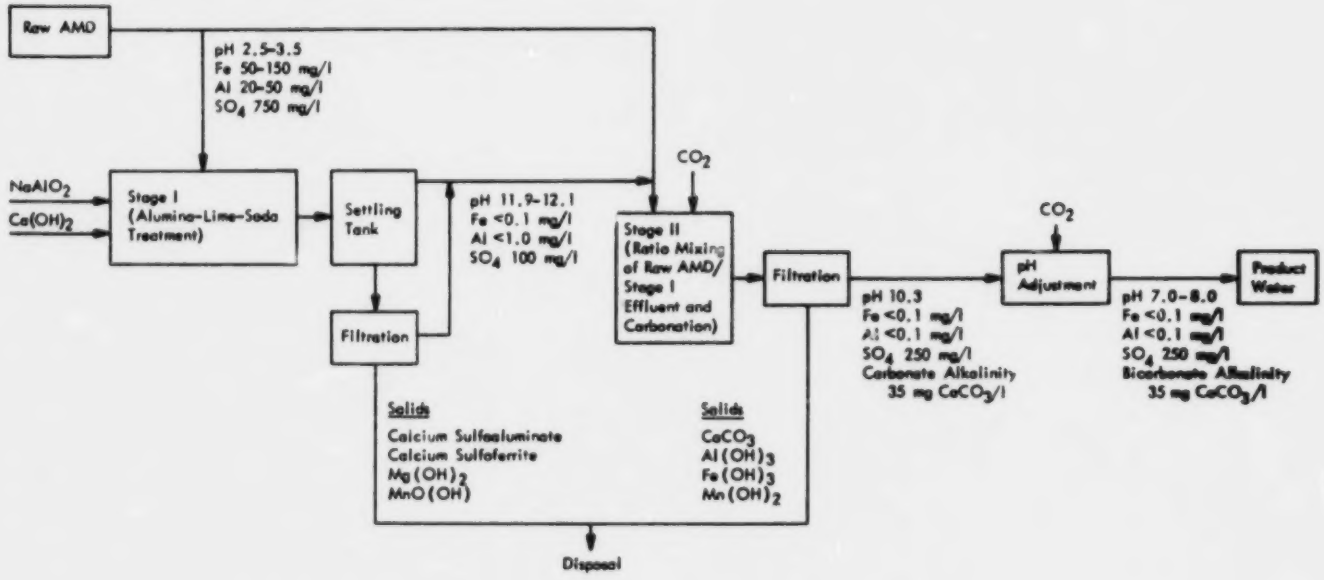


Figure 1. Recovery of potable water from acid mine drainage using the alumina-lime-soda process.

In addition, calcium sulfate will also react with *in situ* iron in the raw water to produce calcium sulfoferrite $CaSO_4 \cdot Fe_2O_3 \cdot 3CaO \cdot xH_2O$. The purpose of the sodium aluminate is to provide the system with sufficient aluminum to reduce sulfate levels to acceptable values, while the lime acts to maintain the pH in the 11.9 to 12.1 range and to stabilize the calcium sulfoaluminate and sulfoferrite precipitates. A sulfate concentration of 100 mg/liter is a practical lower limit for sulfate removal in Stage I.

Following Stage I reaction, the treated mine drainage is allowed to settle, at which time the solids are separated from the effluent. Effluent is sent to Stage II of the process, and settled solids are filtered to recover additional treated water. The alumina-lime-soda solids will settle to a concentration of only about 2%, but can be concentrated to about 10 to 12% by gravity or vacuum filtration. The filtrate recovered represents about 25% of the total Stage I effluent.

Water treated by alumina-lime-soda in Stage I contains excess lime which must be removed in Stage II. The clear effluent from the solids settling and the filtrate removed by solids filtration are mixed with raw acid mine drainage in Stage II to neutralize a part of the excess lime. The proportion of volume between Stage I effluent and raw mine drainage is determined by the sulfate wanted in product water. Effluent from Stage I contains about 100 mg/liter of sulfate. If product water is to contain 250 mg/liter of sulfate, it can be blended with raw acid mine drainage to produce this concentration. This ratio mixing of raw acid mine drainage and Stage I effluent will precipitate the heavy metals in the raw AMD stream.

The mixing of the two streams will not neutralize all the excess lime. Thus, carbon dioxide is added in Stage II to complete neutralization of the lime by precipitating calcium carbonate. Care must be taken in this step of the process to avoid overcarbonating the system. Too much carbon dioxide will redissolve the calcium carbonate precipitate as calcium bicarbonate and result in unneeded hardness in the product water, as well as an unnecessary consumption of carbon dioxide. Therefore, the Stage II carbonation is controlled at a pH of 10.3, the point of minimum solubility of calcium carbonate.

The solids generated in Stage II are separated from the product water by filtration using a sand filter.

The filtrate will have a pH of 10.3 and will contain about 35 mg/liter of dissolved calcium carbonate. The pH of the product is dropped to the 7.0 to 8.0 range by addition of a small amount of carbon dioxide to convert the dissolved carbonate to bicarbonate.

Following this final pH adjustment step, the water recovered from acid mine drainage using the alumina-lime-soda process will meet potable water specifications.

SECTION V

EXPERIMENTAL DEVELOPMENT OF THE PROCESS

GENERAL DISCUSSION

The scheme for using the alumina-lime-soda process to recover water from acid mine drainage described in Section IV has been developed through laboratory studies in a 190 liter/day (50 gal/day) bench-scale pilot unit. A photograph of the assembled unit is presented in Figure 2, together with identification of essential parts. The bench-scale pilot plant consists of:

Stage I

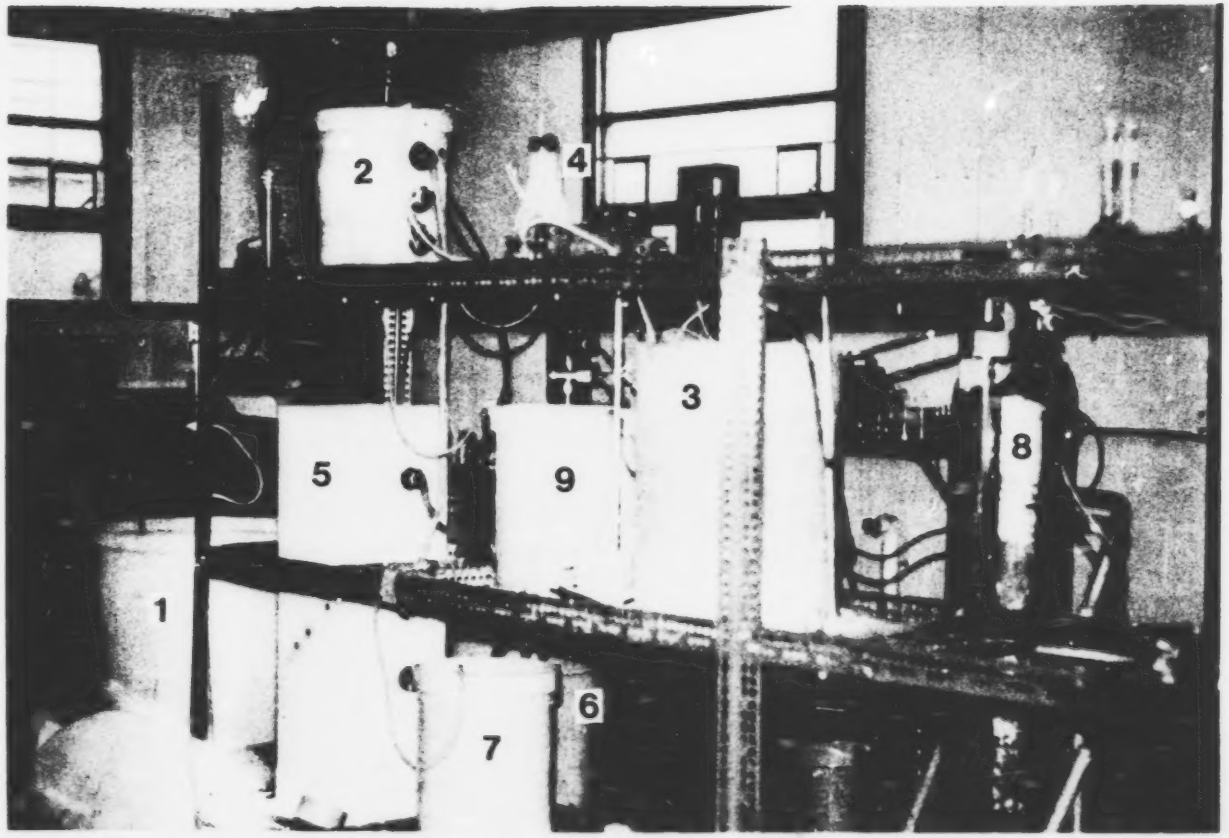
190 liter (50 gal) raw water storage tank;
20 liter (5 gal) Stage I reaction vessel;
40 liter (10 gal) lime storage vessel;
1 liter Erlenmeyer Flask as the sodium/aluminate storage vessel;
70 liter (18 gal) square prism settler; and
20 liter (5 gal) sludge-filtrate collection vessel.

Stage II

20 liter (5 gal) Stage I effluent feed tank;
Size 1A carbon dioxide cylinder; and
20 liter (5 gal) reactor/carbonator vessel.

The system also contains various pumps, stirrers, and flowmeters.

The unit was installed at the Commonwealth of Pennsylvania's Mine Drainage Research Facility, Hollywood, Pennsylvania, in January 1975. Two acid mine drainages available at the Hollywood site were used to develop operating parameters for the alumina-lime-soda process. Average compositions for these mine drainages for the project period are presented in Table 1.



Stage I Alumina-Lime-Soda Treatment

1 Raw AMD Storage Tank
2 Reactor (Stage I)
3 Lime Storage Tank
4 Sodium Aluminate Storage Vessel
5 Settler
6 Stage I Sludge-Filtrate Collection Vessel

Stage II Carbonation

7 Stage I Effluent Storage Tank
8 CO_2 Tank
9 Reactor/Carbonator (Stage II)

Figure 2. Alumina-lime-soda bench-scale pilot plant.

Table 1. AVERAGE COMPOSITION OF HOLLYWOOD, PENNSYLVANIA, ACID MINE DRAINAGES, JANUARY TO JUNE 1975

	Proctor No. 1	Proctor No. 2
pH	3.8	2.8
Acidity, mg/ℓ as $CaCO_3$	180	700
Sulfate, mg/ℓ as SO_4	300	750
Calcium, mg/ℓ as Ca	6	8
Magnesium, mg/ℓ as Mg	15	25
Sodium, mg/ℓ as Na	8	2
Iron, mg/ℓ as Fe total	30	100
Iron, mg/ℓ as Fe^2	Not determined	19
Aluminum, mg/ℓ as Al	20	40

The bulk of the effort was spent in establishing Stage I parameters for the stronger mine drainage, Proctor No. 2. This drainage is more representative of those which are likely candidates for alumina-lime-soda treatment. Experiments with Proctor No. 1 were significant, however, since the different water yielded data which greatly facilitated the interpretation of results, particularly the identification of chemical processes.

After Stage I was established for both Proctors Nos. 2 and 1, the Stage II processes were evaluated. Since the carbonation reaction of Stage II involves straightforward chemical reactions in contrast to Stage I, less emphasis was placed there.

A majority of the experimental data for process development consisted of analyses of aqueous phases at various stages in the process for important constituents. The constituents sought and the analytical methods used are shown in Table 2, together with expected accuracies. The bulk of the constituents were analyzed using Hach Chemical Company Colorimetric Techniques. These methods were chosen because of their rapidity. As a result of the simplified analysis, we could know within an hour what was happening in a particular experiment, and make appropriate changes.

Table 2. ANALYTICAL METHODS FOR FIELD TESTS

Constituent	Method	Accuracy
Total and calcium hardness	EDTA titration	1,000 ± 50 mg/ℓ
Phenolphthalein and methyl orange alkalinity[a/]	Titration with 0.1 N HCl to phenolphthalein and methyl orange end points	1,000 ± 30 mg/ℓ
Acidity	Titration with 0.1 N NaOH to phenolphthalein end point	1,000 ± 50 mg/ℓ
Sulfate	Hach Chemical Company turbidimetric method	1,000 ± 100 mg/ℓ
Total iron	Hach Chemical Company colorimetric method	10 ± 0.5 mg/ℓ
Aluminum	Hach Chemical Company colorimetric method	100 ± 10 mg/ℓ
pH	Beckman pH meter	± 0.05 pH units

a/ Results used to establish the different forms of alkalinity:
Causticity - Principal constituent when most of the total alkalinity is phenolphthalein alkalinity.
Carbonate - Principal constituent when the phenolphthalein alkalinity is about half the total alkalinity.
Bicarbonate - Principal constituent when most of the total alkalinity is methyl orange alkalinity.

In subsequent discussion in this section, we shall present the pertinent data obtained during the experiments. Data presented represent a daily average for a particular run. The average is that obtained from hourly analyses of the effluents from the runs.

The discussion will be organized around particular aspects of the process, i.e., Stage I, Stage II, and Solids Separation.

STAGE I - ALUMINA-LIME-SODA TREATMENT

Experimental Procedures and Observations

The Stage I experiments consisted of the addition of lime and sodium aluminate to the raw acid mine drainage in the 20 liter (5 gal) reactor and allowing the mixture to react for a specified length of time. Reaction time was determined by the flows of the various process streams, and by the position of the overflow port on the Stage I reactor. Following reaction, the sludge was allowed to settle, and the effluent sampled for analysis. In later stages of the program, the effluent was sent to the Stage II reactor where it served as feed in carbonation experiments. Figure 3 shows the lime and sodium aluminate being added to the Stage I reactor.

The lime needed for the reaction in Stage I was added in the following manner: calcium hydroxide (5 g/liter) was added to the raw acid mine drainage in the 40 liter (10 gal) lime storage vessel. This mixture was constantly stirred and pumped into the system by means of a small metering pump. Raw mine drainage was used to carry the lime solution in order to simplify interpretation of results. In most cases, the lime solution constituted about 35 to 40% of the raw water flow through the system.

The sodium aluminate was also added as a solution. Technical grade sodium aluminate (50 g/liter) was dissolved in distilled water and pumped to the Stage I reactor at rates from 1.0 to 1.8 ml/min. During initial stages of the program, we found that sodium aluminate solutions prepared in this manner were unstable; approximately half of the available aluminum in the sodium aluminate precipitated out in the storage flask after a day or two and was not being added into the Stage I reactor. To overcome the instability problem, we stabilized the sodium aluminate solution by adding excess caustic soda.

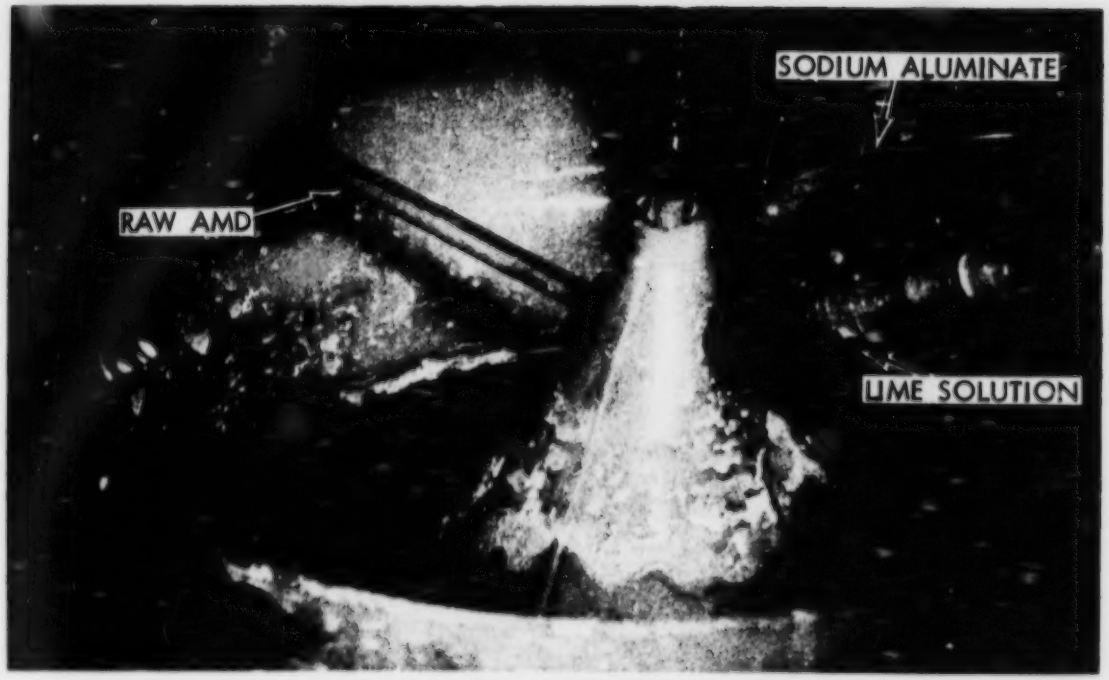


Figure 3. Treatment chemical addition in Stage I reactor.

The Na_2O/Al_2O_3 molar ratio in liquid sodium aluminate is 1.5, whereas the Na_2O/Al_2O_3 ratio in commercial dry sodium aluminate is 1.13 to 1.15. For the process development studies, the sodium aluminate solution was stabilized by adding 12 g of sodium hydroxide pellets for every 100 g of dry sodium aluminate to achieve the 1.5:1 Na_2O/Al_2O_3 ratio found in the liquid sodium aluminate.

The instability of the sodium aluminate was detected by wide variances in sulfate removal. Table 3 compares sulfate removal before and after caustic soda stabilization. The sodium aluminate solution in both cases was a 5% solution at a flow rate of 1.5 ml/min. Before stabilization, the sulfate reduction was quite erratic, whereas the results after stabilization showed a marked increase in removal rate and are relatively nonvariant.

The effluent from the Stage I reactor flowed to the 70-liter (18-gal) settler where the slurry of microcrystalline calcium sulfoaluminate and calcium sulfoferrite formed during the Stage I reaction of raw AMD with lime, and sodium aluminate was allowed to settle out. The effluent from the settler was collected for use in Stage II of the process. The slurry settled rapidly and was easily vacuum-filtered. Figure 4 shows the sludge blanket which forms in the bottom of the settler. For testing purposes only, the slurry was collected and batch-filtered using an Eimco 93 cm^2 (0.1 ft^2) filter leaf with a nylon filament cloth filter.

The sludge generated in the process is readily filtered either by vacuum or sand filtration. (Filtration experimental data appear on p. 29.) The individual precipitate particles seem to form in themselves, i.e., the precipitation reactions are self-seeding. We noticed very little scale buildup on stirrers or reaction vessels during the course of the project. For example, it was never necessary to suspend experiments to clean scale or to unclog piping.

This experience contrasts with conventional lime treatment of AMD in which gelatinous metal hydroxides are troublesome with respect to scaling and clogging. The difference between sludges generated in the alumina-lime-soda process and those in conventional lime treatment is due to the pH conditions at which the sludges are formed. In alumina-lime-soda, the sludges are formed at a pH of 12.0 where they form microcrystals of calcium sulfoaluminate or sulfoferrite. In conventional lime treatment, the sludges are formed at pH's near or below neutrality, and are amorphous since no calcium sulfate and lime are incorporated into them to form the microcrystals.

Table 3. SULFATE REDUCTION WITH AND WITHOUT CAUSTIC SODA STABILIZATION OF SODIUM ALUMINATE

(a) With unstabilized sodium aluminate

Test No.	Percent sulfate removal
2-19	43
2-20	48
2-21	38
2-24	54
2-25	19
2-26	69
2-27	78
2-28	87

(b) With stabilized sodium aluminate

4-3	89
4-7	88
4-8	91
4-10	85
4-11	89
4-16	90

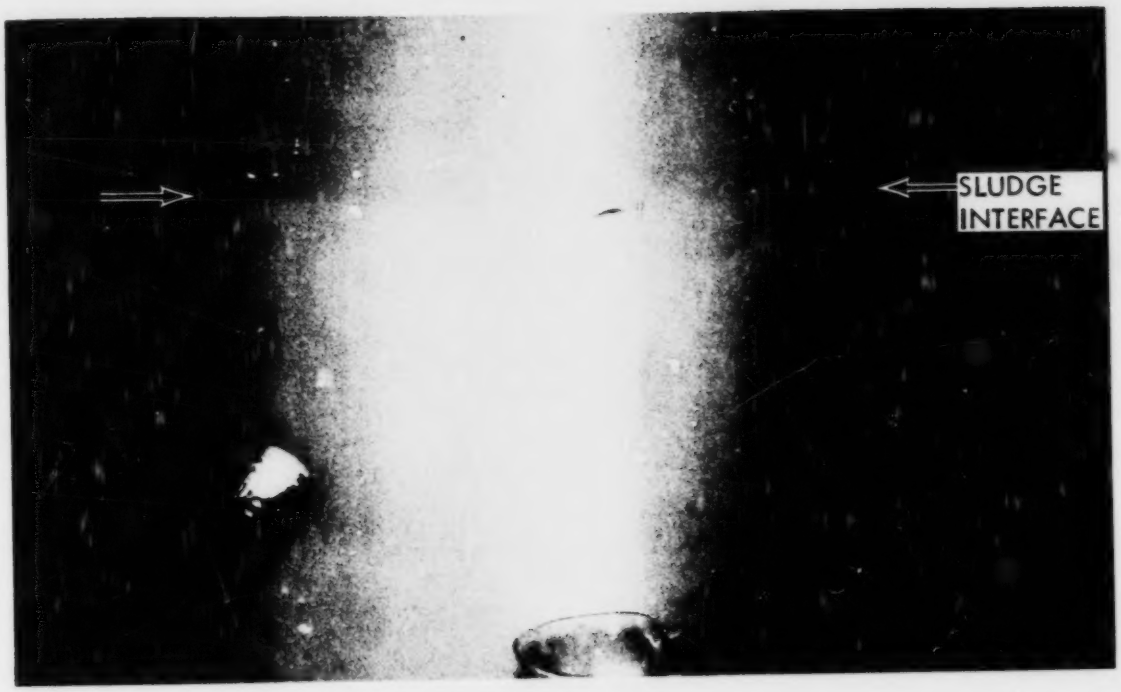


Figure 4. Stage I effluent/sludge interface in settling tank.

Discussion of analytical data obtained for Stage I reactions using Proctors Nos. 2 and 1 mine drainages in continuous runs follows.

Proctor No. 2 Continuous Runs

Data obtained for establishing design parameters for Stage I are presented in Table 4. These data represent those obtained after process consistency was achieved through caustic soda stabilization of sodium aluminate solutions.

The concentrations listed for the addition of lime and sodium aluminate are the calculated concentrations before reaction in Stage I. Calculated concentrations are used so that dosages of the treatment chemicals can be compared directly to concentrations before and after reaction.

The data contained in Table 4 were reduced further so that important process parameters could be identified and quantified. The evaluation of the raw data is discussed in more detail in Section VI of this report.

The data in Table 4 show further that sulfate residuals in Stage I effluent can be reduced to below 100 mg/liter when raw water is treated with sodium aluminate and lime. When the pH of the system drops below 12.0, sulfate concentrations in the treated effluent rise together with aluminum residuals. This observation confirms that the formation of calcium sulfoaluminate is pH-sensitive--a pH of 12.0 is the minimum value for effective sulfate removal.

For process design purposes, it appears that target sulfate residuals should be about 100 mg/liter. If lower concentrations are sought, then the system will require higher pH's. The added costs for lime needed to obtain the higher pH are not worth the minimal sulfate removal benefit. Thus, we have chosen the sulfate level of 100 mg/liter as the target concentration for Stage I effluent.

Table 4. EXPERIMENTAL DATA FOR DESIGN OF STAGE I. RUNS WITH PROCTOR NO. 2 ACID MINE DRAINAGE

Test No.	Raw AMD				Treatment chemicals (calculated values)			
					Sodium aluminate		Lime	
	Acidity (mg/ℓ as $CaCO_3$)	Fe (mg/ℓ)	Al (mg/ℓ)	SO_4 (mg/ℓ)	Causticity (mg/ℓ as $CaCO_3$)	Al (mg/ℓ)	Ca (mg/ℓ as $CaCO_3$)	Causticity (mg/ℓ as $CaCO_3$)
4-2	730	90	40	650	430	130	2,600	2,300
4-3	730	95	40	680	430	130	2,600	2,300
4-7	720	100	45	680	430	130	2,600	2,300
4-8	730	95	60	680	430	130	2,600	2,300
4-10	730	95	50	600	430	130	2,600	2,300
4-11	690	90	60	700	430	130	2,600	2,310
4-16	790	90	40	700	430	130	2,600	2,270
4-17	810	100	40	680	430	130	2,600	2,260
4-22	850	120	45	750	430	130	2,340	2,030
4-23	860	120	45	780	430	130	2,470	2,130
4-24	860	110	50	800	430	130	2,600	2,240
4-25	700	110	60	720	430	130	2,470	2,200
4-28	670	120	65	780	430	130	2,600	2,320
4-29	650	115	60	750	430	130	2,660	2,390
4-30	650	115	60	750	430	130	2,660	2,390
5-5	630	110	60	700	430	130	2,660	2,390
5-28	620	105	40	700	430	130	2,470	2,230
5-29	560	100	40	700	430	130	2,470	2,250
5-30	590	100	40	670	430	130	2,470	2,240
5-31	640	100	ND	690	430	130	2,470	2,220
6-4	690	105	40	720	430	130	2,470	2,200
6-5	660	105	40	690	430	130	2,470	2,210
6-6	680	100	40	700	430	130	2,470	2,200
6-8	690	110	55	800	430	130	2,470	2,200

Table 4. (Concluded)

Test No.	Stage I effluent Fe (mg/ℓ)	Al (mg/ℓ)	SO_4 (mg/ℓ)	Hardness (mg/ℓ as $CaCO_3$)	Causticity (mg/ℓ as $CaCO_3$)	pH	Flow rates Raw AMD (ml/min)	Lime (ml/min)	$NaAlO_2$ (ml/min)	Residence time (min)
4-2	Nil	1.0	90	1,130	920	12.3	100	70	1.70	87
4-3	Nil	0.5	70	930	790	12.2	100	70	1.50	87
4-7	Nil	0.2	80	870	810	12.2	100	70	1.50	87
4-8	Nil	0.3	60	1,140	980	12.4	100	70	1.65	87
4-10	Nil	0.2	90	1,120	950	12.3	100	70	1.50	87
4-11	Nil	0.2	80	1,120	940	ND	100	70	1.50	87
4-16	Nil	0.3	70	1,090	970	ND	100	70	1.50	87
4-17	Nil	0.4	90	1,060	880	ND	100	70	1.50	87
4-22	Nil	2.7	100	900	720	ND	100	60	1.50	93
4-23	Nil	1.1	190	1,000	900	11.9	100	65	1.50	90
4-24	Nil	1.2	170	890	610	11.9	100	70	1.50	87
4-25	Nil	0.2	170	700	620	12.0	100	65	1.50	90
4-28	Nil	1.7	160	830	610	11.8	100	70	1.50	87
4-29	Nil	2.6	180	1,010	650	11.7	100	75	1.50	85
4-30	Nil	1.3	170	1,350	750	11.0	100	75	1.50	85
5-5	Nil	1.4	140	1,070	700	11.8	100	75	1.50	85
5-28	Nil	ND	80	1,250	970	12.0	100	65	1.50	90
5-29	Nil	ND	50	1,030	910	12.0	100	65	1.50	90
5-30	Nil	ND	130	1,050	740	12.0	100	65	1.50	90
5-31	Nil	ND	140	1,240	840	11.9	100	65	1.50	90
6-4	Nil	1.3	130	760	580	11.8	100	65	1.50	90
6-5	Nil	0.3	160	1,180	730	11.8	100	65	1.50	90
6-6	Nil	1.1	160	760	600	ND	100	65	1.50	90
6-8	Nil	0.4	190	940	630	ND	100	65	1.50	90

ND = Not determined.
Nil = 0.1 mg/

The hardness and causticity data for Stage 1 effluent as shown in Table 4 are indicative of reactions with the lime. The difference between hardness and causticity in the effluent is a measure of how much noncarbonate hardness is left in the treated water. Noncarbonate hardness in treated acid mine drainage is due to calcium sulfate. Thus, the smaller the difference between hardness and causticity, the greater has been the removal of calcium sulfate. We note in the data that differences between hardness and causticity are relatively constant at pH's above 12.0. However, absolute levels of hardness and causticity increase with increasing pH, a phenomenon which is expected. This observation implies that the minimum quantity of lime needed for the alumina-lime-soda process is that which maintains the pH at 12.0. If more lime is present than the minimum, it serves no useful purpose in the process chemistry.

As can be seen from the data in Table 4, the hardness and causticity levels in Stage I effluent vary considerably. However, the minimum causticity level where sulfate is effectively removed is on the order of 600 mg/liter as $CaCO_3$. This causticity value will maintain the Stage I reaction pH at 12.0.

Thus, it can be concluded that sufficient lime must be added to maintain minimum pH and causticity levels; excess lime is unnecessary and will increase processing costs. The costs are increased in two ways. First is the cost of excess lime and second is the cost of the carbon dioxide needed to neutralize the excess lime. Therefore, it is important to control the Stage I reactions by means of maintaining the pH at 12.0 and the causticity level of 600 mg/liter by the use of lime.

Residence times were varied during shake-down experiments early in the program. These experiments indicated that the minimum residence in Stage I needed for maximum sulfate removal was in the 80- to 100-min range. Thus, a residence time of approximately 90 min was chosen for the design experiments reported in Table 4.

The relatively long residence times needed for the Stage I reactions and the fact that the reactions were conducted while exposed to air resulted in the complete oxidation of ferrous iron in the raw AMD to ferric oxide. The ferric oxide in turn appeared to react with calcium sulfate to precipitate a calcium sulfoferrite. The oxidation of ferrous iron to ferric iron could be observed in the lime storage vessel. When lime was first added to the raw AMD, a dark blue-green precipitate formed due to ferrous iron. As the mixture was stirred, the color of the precipitate changed from

blue-green to brown and finally to a rust color normally associated with ferric hydroxide. This color change was virtually complete within 1 hr.

Proctor No. 1 Continuous Runs

Table 5 lists the analyses for tests conducted using Proctor No. 1 acid mine drainage. This water is much more dilute than Proctor No. 2. The data were obtained and analyzed in the same manner as described for Proctor No. 2.

Again the lime, sodium aluminate, and raw acid mine drainage were combined in the Stage I reactor. The reaction products were discharged to the settler where the sludge was removed. The effluent was analyzed for constituents of interest. The concentrations of the treatment chemicals were reduced for the Proctor No. 1 experiments, so that flow rates and residence times would be similar to those used for the Proctor No. 2 studies. Sodium aluminate was added as a 1.6% solution stabilized with 1.9 g/liter of caustic soda. Lime was added as a 0.2% solution.

The most significant fact disclosed by the tests with Proctor No. 1 was the rate for lime in the system. Causticity of the Stage I effluent was consistently below 600 mg/liter and sulfate levels never fell below 100 mg/liter. Further, pH of Stage I effluent rarely was 12.0 and larger aluminum residuals were noted when pH was below 12.0. These observations suggest that sulfate was not being removed because insufficient lime was present to form stable calcium sulfoaluminate. The results imply that the lime in alumina-lime-soda prefers to react with calcium sulfate and aluminate ion to form the calcium sulfoaluminate sludge. Sludge formation consumes lime, thus making it unavailable for pH control. Closer examination of the Proctor No. 1 raw water indicated that magnesium was proportionally much higher in the Proctor No. 1 than in Proctor No. 2. Thus, a greater amount of the lime was reacting with magnesium in the case of Proctor No. 1 than in Proctor No. 2, and insufficient lime was being added to form the sludge and to maintain pH and causticity requirements.

Table 5. EXPERIMENTAL DATA FOR DESIGN OF STAGE I. RUNS WITH PROCTOR NO. 1

Test No.	Raw AMD				Treatment chemicals			
					Sodium aluminate		Lime	
	Acidity (mg/ℓ as $CaCO_3$)	Fe (mg/ℓ)	Al (mg/ℓ)	SO_4 (mg/ℓ)	Causticity (mg/ℓ as $CaCO_3$)	Al (mg/ℓ)	Ca (mg/ℓ as $CaCO_3$)	Causticity (mg/ℓ as $CaCO_3$)
5-12	150	15	20	300	140	40	1,060	1,000
5-13	170	25	15	320	140	40	1,060	990
5-14	160	25	40	280	110	40	1,060	990
5-15	180	35	25	300	110	40	1,060	990
5-16	170	30	20	350	140	40	1,060	990
5-17	180	20	30	300	140	55	1,110	1,030
5-19	170	20	30	280	140	55	1,110	1,040
5-20	180	35	25	320	140	55	1,110	1,030
5-15A	180	35	25	300	110	40	1,060	990
5-16A	170	30	20	350	140	40	1,060	990
5-17A	180	20	30	300	140	55	1,110	1,030
5-19A	170	20	30	280	140	55	1,110	1,040
5-20A	180	35	25	320	140	55	1,110	1,030

Test No.	Stage I effluent						Flow rates			Residence time (min)
	Fe (mg/ℓ)	Al (mg/ℓ)	SO_4 (mg/ℓ)	Hardness (mg/ℓ as $CaCO_3$)	Causticity (mg/ℓ as $CaCO_3$)	pH	Raw AMD (ml/min)	Lime (ml/min)	$NaAlO_2$ (ml/min)	
5-12	Nil	4.5	140	910	530	11.5	100	75	1.50	85
5-13	Nil	3.4	140	1,020	550	11.7	100	75	1.50	85
5-14	Nil	6.2	140	860	480	11.9	75	56	1.20	113
5-15	Nil	2.2	150	1,020	540	12.0	75	56	1.20	113
5-16	Nil	4.0	140	830	480	11.9	75	56	1.50	113
5-17	Nil	18.7	190	610	240	11.4	75	60	1.50	110
5-19	Nil	20.0	170	800	400	11.5	75	60	1.50	110
5-20	Nil	1.6	120	1,020	610	12.0	75	60	1.50	110
5-15A	Nil	1.3	160	880	480	12.0	75	56	1.20	189
5-16A	Nil	2.1	140	790	450	11.9	75	56	1.50	189
5-17A	Nil	11.8	170	570	250	11.5	75	60	1.50	183
5-19A	Nil	7.4	170	610	290	11.4	75	60	1.50	183
5-20A	Nil	1.4	110	930	560	12.0	75	60	1.50	183

Nil = < 0.1 mg/ℓ.

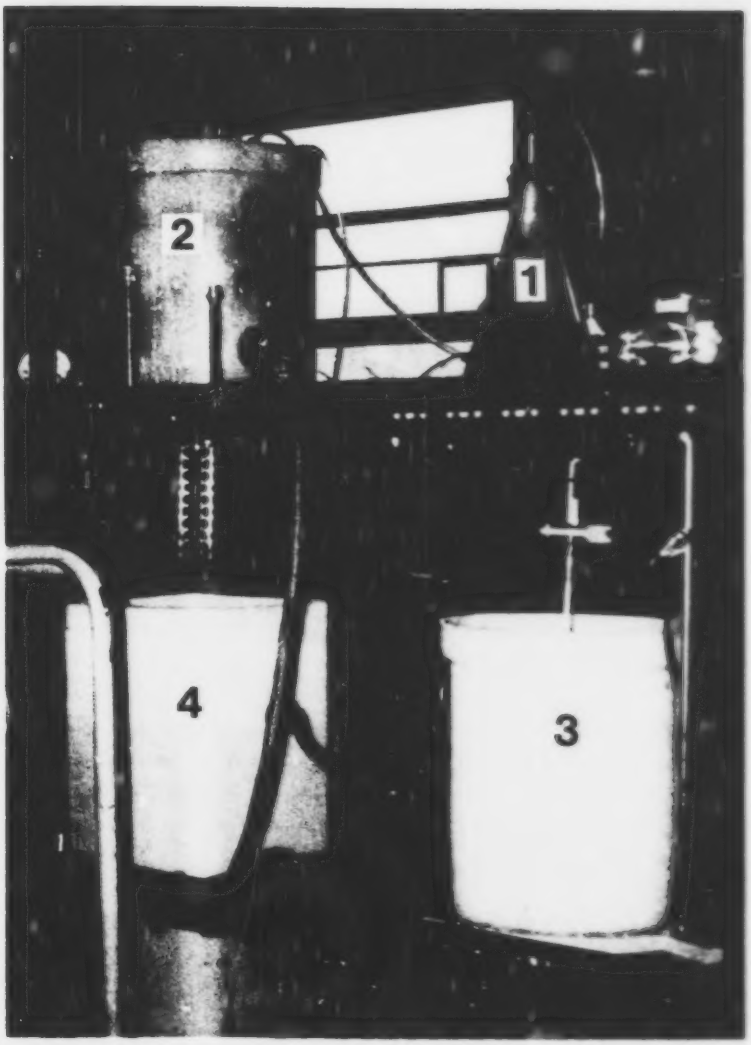
During the testing of Proctor No. 1, extended residence times were tried to see if insufficient reaction time was responsible for the poor sulfate removal. These studies (5-15A through 5-20A in Table 5) were conducted by placing two of the 15-liter (5-gal) reactors in series as shown in Figure 5. Data from the experiments indicate that extended residence time has little effect on the sulfate removal in Stage I of the alumina-lime-soda process. It is concluded therefore that sulfate removal is more dependent on sufficient lime to maintain the pH at 12.0 and causticity at 600 mg/liter than it is on residence time.

STAGE II - RATIO MIXING OF RAW AMD/STAGE I EFFLUENT AND CARBONATION

The tests on Stage II were conducted with Proctor No. 2 acid mine drainage. The treated, filtered water from Stage I was collected in a holding tank, and the water was then mixed with raw AMD in the proper ratio before carbonation. The treated and raw AMD are mixed in such a ratio that the final sulfate level is 250 mg/liter or less, which meets the USPHS limits. The mixing of the two waters also allows the acid in the raw AMD to partially neutralize the hydroxide alkalinity in the effluent water. By mixing with the raw AMD we also reduce the amount of CO_2 needed in the process.

The effluent from Stage I for Proctor No. 2 AMD has a sulfate level of approximately 100 mg/liter, the raw AMD has a sulfate level of approximately 700 mg/liter. Based upon this, the calculated ratio to yield 250 mg/liter sulfate would be 5 parts of treated AMD to 1 part raw AMD for Proctor No. 2.

A series of different ratios were tried to establish the principle of ratio mixing. The results are presented in Table 6. The alkalinity levels are lower in the effluent than calculated, probably due to the reaction of Stage I effluent with magnesium in the raw AMD. The differences between actual and calculated sulfate levels are within reasonable limits for the accuracy of the analytical method. Based on these results, the optimum ratio for Proctor No. 2 would be about 3 parts of raw AMD to 1 part of treated effluent.



Stage I Alumina-Lime-Soda Treatment

1) Sodium aluminate storage vessel
2) Reactor (Stage I)
3) Reactor (Stage I) for extended residence time
4) Settler

Figure 5. Additional reaction vessel for extended residence time studies.

Table 6. RATIO MIXING OF STAGE I EFFLUENT AND PROCTOR NO. 2 ACID MINE DRAINAGE

	Acidity	Alkalinity, mg/ℓ		SO_4, mg/ℓ	
		Actual	Calculated	Actual	Calculated
Raw AMD	730	00	-	680	-
Stage I effluent	00	930	-	90	-
Parts mixed					
Stage I: raw AMD					
1:1	00	30	200	440	385
2:1	00	280	377	400	288
3:1	00	430	515	260	240
5:1	00	550	653	200	191

The two streams were mixed as they entered the carbonator, which has a 10-liter capacity. The CO_2 was then added to the reactor through a bubbler tube at the bottom of the vessel. The acidity of the raw AMD neutralizes some of the hydroxide alkalinity, which reduces the amount of CO_2 required in the first carbonation. The CO_2 must be added to reduce the pH to 10.3, the point of minimum calcium carbonate solubility (about 35 mg/liter). Lowering the pH below 10.3 will result in the redissolution of calcium carbonate, manifested by an increase in the bicarbonate alkalinity and a decrease in the carbonate alkalinity. If the pH is above 10.3, the system will contain free hydroxide alkalinity (causticity). The chemistry described above is analogous to that encountered in conventional lime-soda ash softening.[2/]

Table 7 shows the concentrations of constituents in effluents from the Stage II (carbonator) reactor. The small size of the bench-scale unit made carbonation very difficult to control. The only way to achieve this pH control was by turning the CO_2 on and off for various lengths of time. In all the tests, some excess CO_2 was introduced, resulting in pH's less than 10.3 and in undesired bicarbonate alkalinity. However, the tests numbered 6-5 and 6-6, where the pH approached 10.0, show that as we approach the pH of 10.3, we will be able to achieve the maximum removal of $CaCO_3$. By achieving minimum values of carbonate alkalinity, we will remove the maximum amount of $CaCO_3$, and the amount of CO_2 needed in the pH adjustment step will be minimized.

Table 7. EXPERIMENTAL DATA FOR DESIGN OF STAGE II RUNS WITH PROCTOR NO. 2

Test No.	Concentration CO_2 effluent							Flow rates	
	Fe (mg/ℓ)	Al (mg/ℓ)	SO_4 (mg/ℓ)	Hardness (mg/ℓ as $CaCO_3$)	Carbonate alkalinity (mg/ℓ as $CaCO_3$)	Bicarbonate alkalinity (mg/ℓ as $CaCO_3$)	pH	Raw AMD (ml/min)	Treated AMD (ml/min)
4-23	Nil	2.3	260	330	70	25	9.0	33	165
4-24	Nil	0.9	340	600	55	155	8.7	33	165
4-25	Nil	0.1	260	280	00	335	7.4	29	140
4-28	Nil	1.7	250	250	45	55	9.1	33	165
4-29	Nil	2.6	230	290	30	55	9.4	33	170
4-30	Nil	2.8	240	250	30	00	9.6	33	170
5-5	Nil	1.8	240	290	20	145	8.2	33	175
5-28	Nil	0.5	160	270	00	140	8.2	33	165
5-29	Nil	0.8	150	260	00	210	7.7	33	165
5-30	Nil	0.9	160	160	00	210	8.6	34	165
5-31	Nil	1.1	170	220	00	120	8.3	34	165
6-4	Nil	1.4	230	300	00	100	8.1	33	165
6-5	Nil	4.2	180	160	25	00	9.9	33	165
6-6	Nil	2.8	260	330	25	00	9.8	33	165
6-8	Nil	2.7	250	240	45	55	9.2	33	165

Nil = < 0.1 mg/ℓ.

STAGE I - SLUDGE CHARACTERIZATION

The calcium sulfoaluminate and sulfoferrite solids generated in Stage I of the alumina-lime-soda process produce a sludge which is filtered to recover water. The following discussion contains data obtained from experiments dealing with sludge filtration and settling.

Filtration Analysis

The filtration analysis was necessary to develop an effective method of treating the bulk phase solids from the settler to recover liquids and produce a solid material suitable for handling and disposal. Two filtration methods were evaluated for use in the 190,000 liter/day (50,000 gal/day) pilot plant--sand and vacuum. Vacuum filtration is expensive in both capital requirements and operating techniques. For small plants, i.e., the 190,000 liter/day (50,000 gal/day) demonstration plant described in Appendix A, the sand filter is preferred, despite the fact that filtration rates are much slower. The following discussion presents findings of the sand and vacuum filtration experiments.

Sand Filtration Experiments - Sand filter tests using a graded sand and gravel medium were conducted in a 6-in. diameter plexiglas column to determine the filtration rate, rate of cake buildup on the sand, and solids separation efficiency. The solids concentration in the feed solution was approximately 1.9%. The rates of filtration and cake buildup are shown in Figure 6 as they vary with the volume of solution filtered. An average filtration rate of 1,600 liters/day/m^2 (40 gal/day/ft^2) of filter area was obtained, which corresponds to a solids filtration rate, or solids loading, of 31 kg/m^2/day (6.3 lb/ft^2/day) at a 1.9% solid concentration in the feed slurry. The solids include water of hydration associated with the chemical composition of the calcium sulfoaluminate/sulfoferrite sludge. The cake buildup on the filter was determined to be about 2.5 cm/hr (1.0 in./hr) based upon cake buildup and flow rate curves in Figure 6.

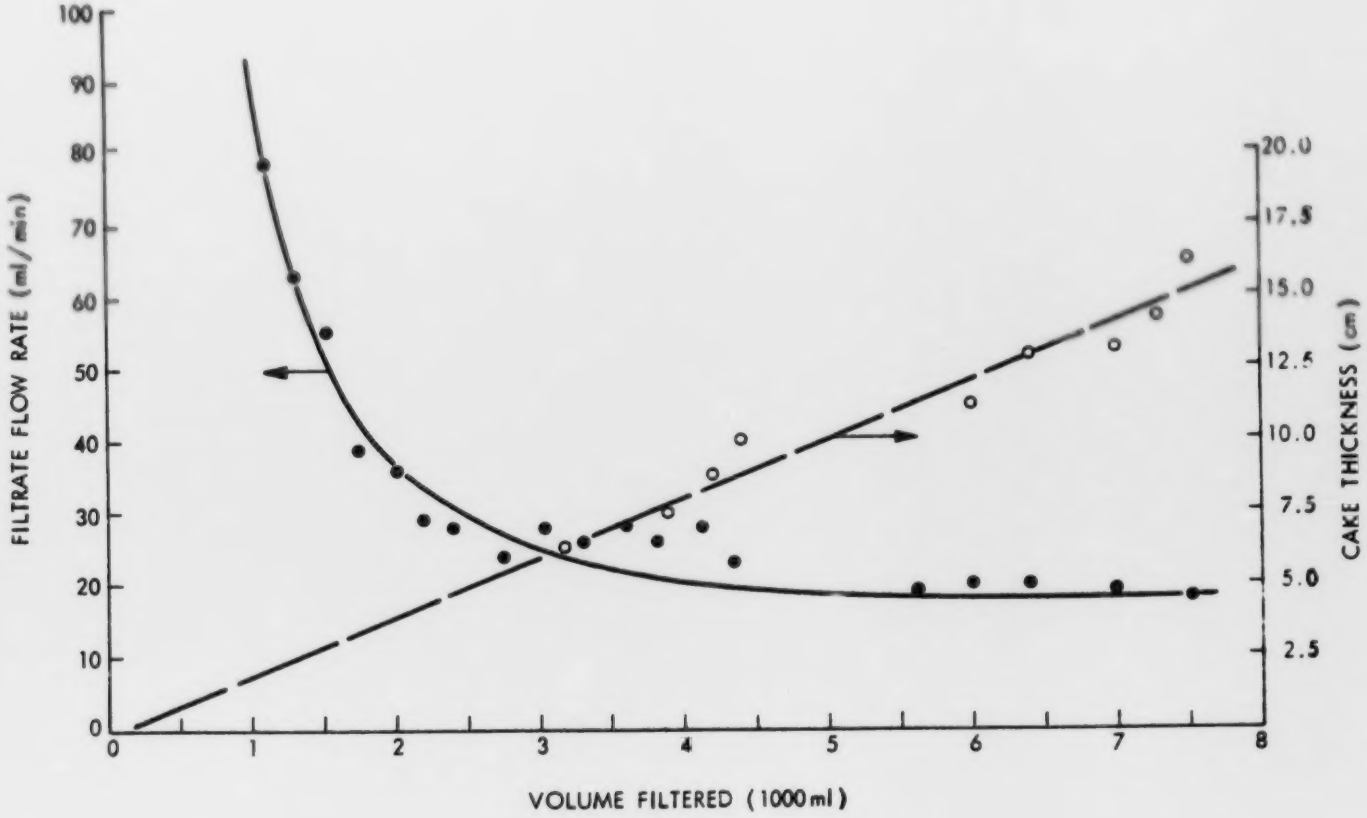


Figure 6. Sand filtration of solids phase from settler.

The solids collected on the surface of the sand filter were of a thick-paste consistency. The dry solids content of the filter cake was about 10%. When removed from the filter, the solids did not flow due to their microcrystalline nature. Thus, the solids should be readily handled for disposal, since they do not exhibit characteristics normally associated with amorphous sludges and slimes.

The suspended solids content in the clear filtered effluent was nearly zero.

Vacuum Filter Experiments - Vacuum filter experiments were conducted using an Eimco 9.3 cm^2 (0.1 ft^2) filter leaf to determine vacuum filtration rates. Table 8 shows the vacuum filtration data obtained from the experiments.

The filter yield, B , is the rate of solids filtered per unit area, which is given by the following expression.

$$B = \left[\frac{2 \times P \times W \times \alpha}{\mu \times R \times t_c}\right] 1/2 \qquad (5\text{-}1)$$

where P = vacuum pressure, g/cm^2

W = mass of solids filtered per unit volume of filtrate, g/ml

$\alpha = t_f/t_c$, form time per cycle time, sec/sec = dimensionless

μ = filtrate viscosity, g/cm-sec

R = specific resistance, sec^2/g

t_c = cycle time, sec

t_f = form time, sec

Table 8. VACUUM FILTRATION DATA

Filtration measurements	
Time (sec)	Volume (ml)
60	1,200
120	1,800
165	2,000

Filtration parameters

Vacuum pressure, mm Hg	597
P = Vacuum pressure, g/cm^2	811
C_i = Initial solids concentration, %	1.9
C_f = Final solids concentration in cake, %	11.7
A = Filtration area, cm^2	93
t_c = Cycle time, sec	165
t_f = Form time, sec	120
μ = Viscosity, g/cm-sec	0.009
Total filtrate volume, ml	2,000

The mass of solids filtered per unit volume of filtrate, W, is calculated by the following equation.

$$W = \frac{P}{\frac{(100 - C_i)}{C_i} - \frac{(100 - C_f)}{C_f}} \qquad (5\text{-}2)$$

where P = density of filtrate, g/ml

C_i = initial solids concentration, %

C_f = final solids concentration in cake, %

The specific resistance is calculated by plotting the time per unit volume of filtrate versus the filtrate volume. This plot of experimental data is shown in Figure 7. The slope of the line, b, must be used in the following equation to calculate the specific resistance.

$$R = \frac{2 \times b \times P \times A^2}{\mu \times W} \qquad (5\text{-}3)$$

where A = filter area

Other factors are the same as those defined above.

Substituting the values in Table 8 into the various equations, and using specific resistance, R, as determined by Figure 7, it is found that:

$B = 3.03 \times 10^{-3}$ g/cm^2/sec

$= 2{,}600$ kg/m^2/day

$= 535$ lb/ft^2/day

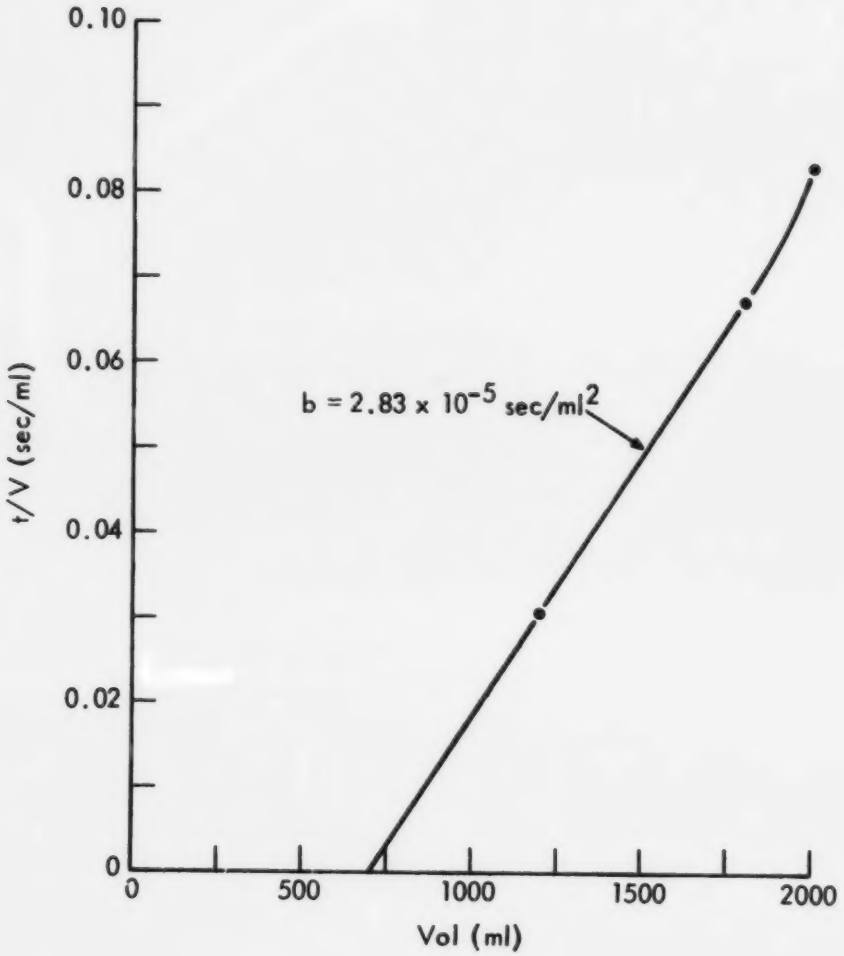


Figure 7. Vacuum filtration specific resistance plot.

Settling Analysis

The purpose of the settling study was to determine if the solids could be separated effectively by settling. If so, what would be the residence time and solids contents of the supernatant and sludge? The solids produced in the reactor settle as a bulk phase at the high concentrations obtained (0.6%); whereas discrete particle settling is obtained at low solids concentrations. Bulk phase settling can be characterized by measuring the settling velocity of the solid-liquid interface. The solids settle freely until the solids concentration in the bulk phase becomes high enough that compression begins. At this point, the settling velocity decreases sharply.

Figure 8 shows a plot of the height of the interface versus settling time. The settling occurred in a cylindrical container having a cross-section of 0.06 m^2 (0.66 ft^2), which contained reactor effluent with an initial solids concentration of 0.6%. A constant settling rate of 1.8 cm/min (0.7 in/min) occurred for the first 5 min. Solids compression began after 10 min, diminishing the settling rate accordingly.

The solids concentrations in the bulk solid and liquid phases were measured following settling. The supernatant liquid concentration was 0.02%, and the bulk solid phase was 1.89% solids. The bulk solids phase contains material which is filtered to recover Stage I effluent.

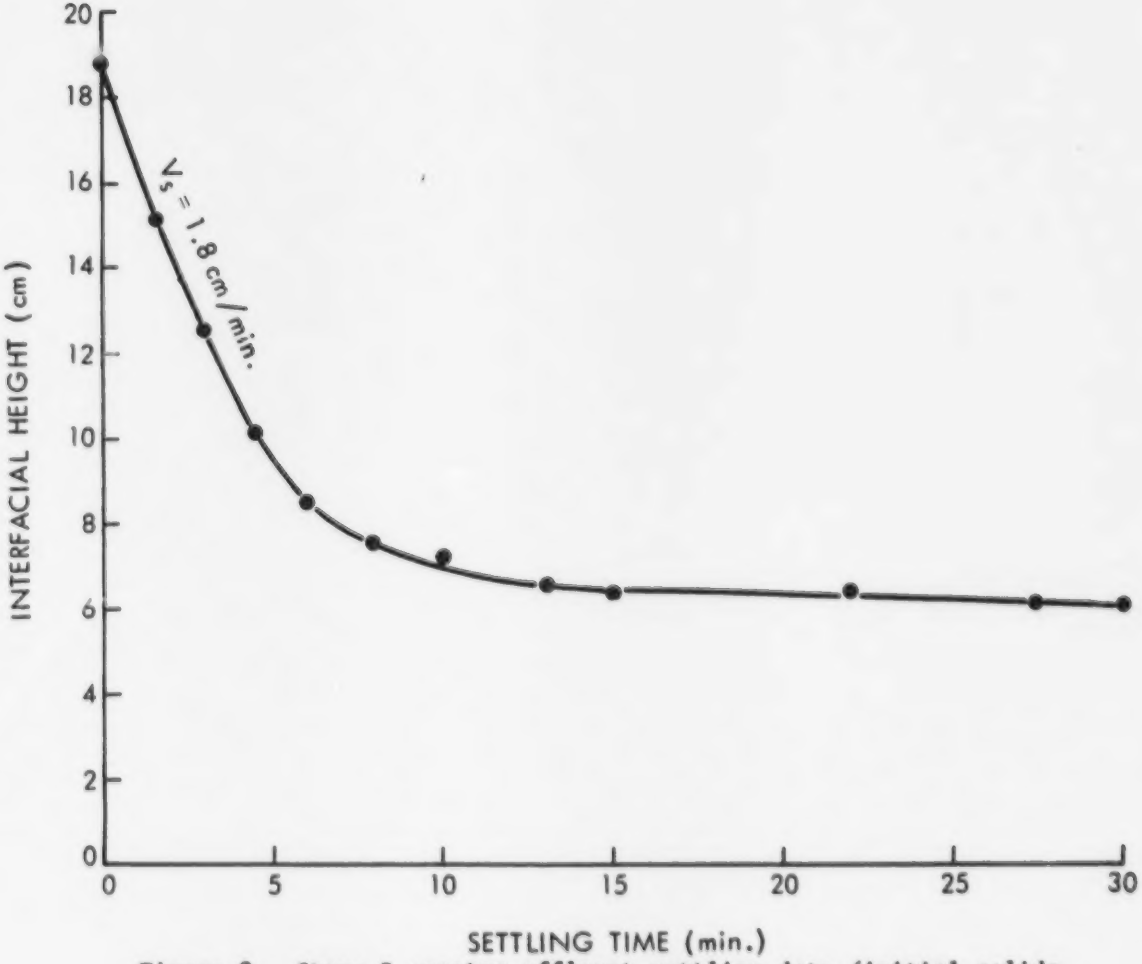


Figure 8. Stage I reactor effluent settling data (initial solids concentration equal to 0.6%).

SECTION VI

DATA INTERPRETATION AND DISCUSSION

REDUCTION OF EXPERIMENTAL DATA

The raw data presented in Tables 4 and 5 have been interpreted in terms of sulfate and calcium removed in Stage I of the alumina-lime-soda process as functions of total iron and aluminum inputs and of causticity of the Stage I effluent. Molar ratios of sulfate/(iron + aluminum) and calcium/(iron + aluminum) have been calculated, in which metal used is the sum of the *in situ* iron and aluminum, and aluminum added as sodium aluminate. These ratios have been plotted against the causticity of Stage I effluent and are shown in Figures 9 and 10.

The shape of the curves in Figures 9 and 10 indicate that both sulfate removal and calcium removal is stabilized when causticity of Stage I effluent reaches about 600 mg/liter. Thus, causticities (from lime addition) in Stage I effluent above 600 mg/liter represent unnecessary use of lime, which in turn will increase carbon dioxide requirements in Stage II. For this reason, the process has been designed around a causticity of 600 mg/liter (as $CaCO_3$) in Stage I effluent.

The 600-mg/liter breakpoint corresponds with a sulfate/(iron + aluminum) ratio of about 0.8, and a calcium/(iron + aluminum) ratio of about 2.2. These ratios suggest a stoichiometry in the Stage I sludge of:

$$0.8SO_3 \cdot 0.5R_2O_3 \cdot 2.2\ Ca \qquad (6\text{-}1)$$

where SO_3 = sulfate (anhydride)

R_2O_3 = iron + aluminum

Ca = calcium

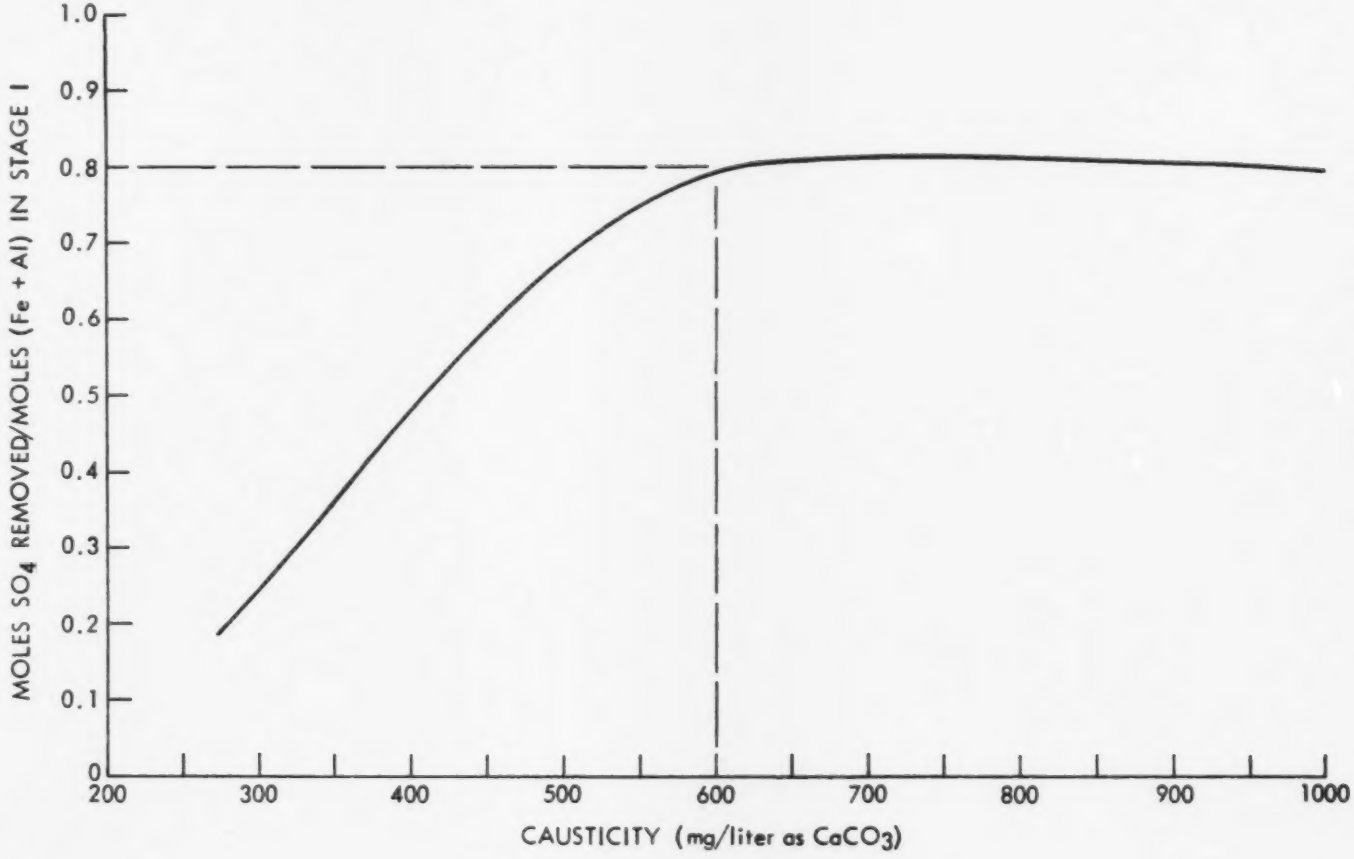


Figure 9. Sulfate removal plotted against causticity in Stage I effluent.

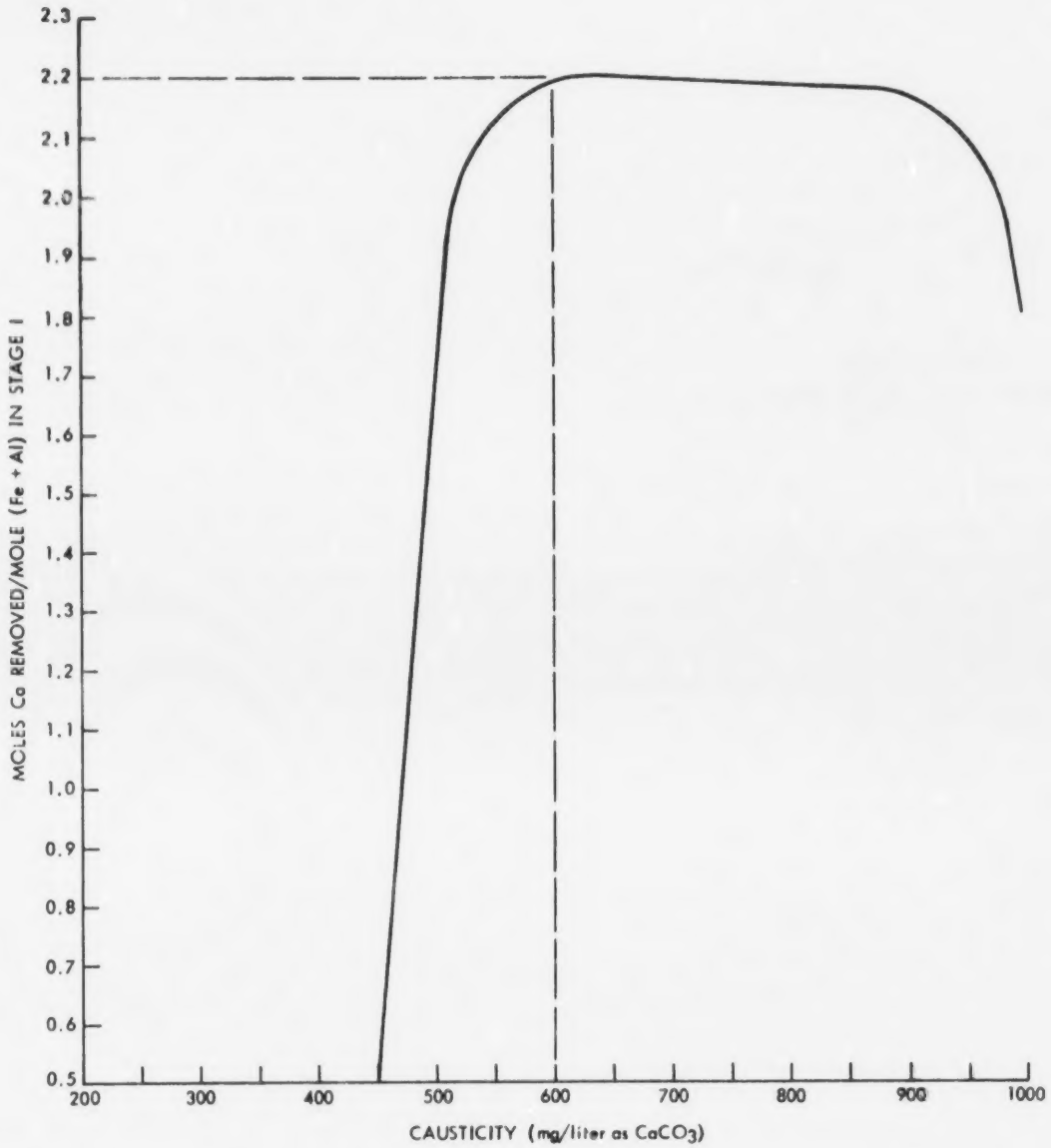


Figure 10. Calcium in sludge plotted against causticity in Stage I effluent.

The coefficient of R_2O_3 is 0.5, since each mole of R_2O_3 contains two moles of metal. If the calcium is distributed between sulfate and oxide (and coefficients multiplied by 10 to clear decimal points), the following stoichiometry of Stage I sludge is established.

$$8CaSO_4 \cdot 5R_2O_3 \cdot 14CaO \qquad (6\text{-}2)$$

Closer examination of the data indicated that some sodium oxide was probably present in the sludge. As will be shown later, the high-sulfate and low-sulfate forms of calcium sulfoaluminate and sulfoferrite consistently have CaO/R_2O_3 ratios of 3.0. Thus, it is likely that a more proper representative of the Stage I sludge stoichiometry is:

$$8CaSO_4 \cdot 5R_2O_3 \cdot 14CaO \cdot Na_2O \qquad (6\text{-}3)$$

In this case, the extra mole of base needed to obtain the CaO/Al_2O_3 ratio of 3.0 is found as Na_2O originally present as sodium aluminate.

The amount of sodium oxide in the sludge appears to be quite variable. A plot of sodium oxide/trivalent metal ratios yielded a set of points too scattered to indicate a clear trend. Thus, it is likely that the composition of the Stage I sludge is more accurately represented:

$$8CaSO_4 \cdot 5R_2O_3 \cdot 15(CaO,\ Na_2O) \qquad (6\text{-}4)$$

Conclusions concerning the effect of the two sources of trivalent metals on the sludge stoichiometry are discussed below.

In the case of Stage I reactions, the iron and aluminum can be obtained from two sources: that contained in the raw AMD (in situ iron and aluminum), and that added as sodium aluminate. In order to separate the effect of in situ iron and aluminum from that of the sodium aluminate, experiments were conducted using solutions of iron sulfate and aluminum sulfate in the MRI Kansas City laboratories. These experiments indicated that when iron sulfate (either ferrous or ferric) was treated with lime, sulfate was removed in approximately an 0.5 sulfate-iron ratio. In a pure aluminum sulfate solution, sulfate was removed in a 1.5 sulfate-aluminum ratio. In mixed iron-aluminum systems, however, the sulfate/(iron + aluminum) ratio of the sludge was about 0.6, indicating that in situ aluminum, when

mixed with *in situ* iron, is less effective for sulfate removal than is pure aluminum sulfate. Thus, we conclude that each mole of *in situ* iron and aluminum will remove about 0.5 mole of sulfate. The remaining sulfate is removed by aluminum added as sodium aluminate.

With this information, it was possible to reduce the empirical formula (6-1) of the sludge to its components, one component being that generated by *in situ* metals, and a second component generated by sodium aluminate. In the case of Proctor No. 2 data, the *in situ* iron and aluminum constituted about 40% of the total trivalent metals. The constituent ratios in (6-4) were adjusted by assuming that each mole of *in situ* metals would remove 0.5 mole of sulfate, and subtracting the appropriate constituents to isolate the effect of aluminum in sodium aluminate (60% of the total trivalent metal content of the system). This exercise yielded a composition of:

$$2CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O) \qquad (6\text{-}5)$$

This empirical formula can be reduced further to equal amounts of the so-called "high-sulfate form" and "low-sulfate form" calcium sulfoaluminates.[3/] Discussion of these two forms of sulfoaluminates follows on p. 42.

$$2\left[2CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O)\right] \longrightarrow$$

$$CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O)\text{(low-sulfate form)} + \qquad (6\text{-}6)$$

$$3CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O)\text{(high-sulfate form)}$$

The preceding interpretation is based on results obtained with Proctor No. 2 acid mine drainage. It is likely that the proportion of high-sulfate and low-sulfate forms of calcium sulfoaluminate produced by sodium aluminate will vary from one mine drainage to another. In general, we would expect that the less iron in raw acid mine drainage, the greater the sulfate removal by sodium aluminate. As will be shown in the following discussion, sodium aluminate will remove more sulfate per mole of aluminum in other systems where iron is absent in the raw water.

RELATION OF SLUDGE STOICHIOMETRY TO OTHER SYSTEMS

The alumina-lime-soda process has the ability to remove calcium sulfate from the water through the precipitation of calcium sulfoaluminate materials having general compositions.

$$xCaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot yH_2O \qquad (6\text{-}7)$$

The calcium sulfoaluminates have been known for many years; they are insoluble materials which prevent "flash set" of portland cement concrete. Indeed, gypsum is added to portland cement for the specific purpose of combining with calcium aluminate in the hydration process to retard the concrete set. As a result, practically all data in the technical literature pertaining to the calcium sulfoaluminate are associated with concrete hardening reactions.

Two forms of calcium sulfoaluminate are recognized as being very important in the set of concrete, and have been well characterized.[3/] The two forms differ with respect to their sulfate-aluminum molar ratios. The so-called "high-sulfate" form has the composition:

$$3CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot 31H_2O \qquad (6\text{-}8)$$

In this case, the sulfate-aluminum molar ratio is 1.5. This material, also known as ettringite, is the stable species when aluminate ion reacts with calcium sulfate in a large excess of lime, such as would be found in an ordinary mixture of portland cement and water. The second calcium sulfoaluminate is referred to as the "low-sulfate" form and has the composition:

$$CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot 12H_2O \qquad (6\text{-}9)$$

In this second case, the sulfate-aluminum ratio is only 0.5, since 1 mole of calcium sulfate is associated with 1 mole of Al_2O_3 containing two atoms of aluminum. Normally, this material is not found after cement has hardened.

In addition to the calcium sulfoaluminates, calcium sulfoferrites have also been reported. However, these materials are less well characterized. The principal calcium sulfoferrites are the ferric oxide (Fe_2O_3) analogues of the high-form and low-form calcium sulfoaluminates.[4/] The principal reason for the lack of characterization of the sulfoferrites appears to be due to the relative unimportance of the iron constituents in portland cement, and to the relative insolubility of iron oxide compared to aluminum oxide.

Contrary to the portland cement system where calcium sulfate and aluminate must be dissolved in limited amounts of water, the alumina-lime-soda system involves the removal of dissolved sulfate from water very much in excess. Thus, the virtual instantaneous formation of calcium sulfoaluminate in the portland cement-water system does not occur in the alumina-lime-soda process. As a result, about a 90 min residence time is needed in the alumina-lime-soda process to complete formation of calcium sulfoaluminate.

In the case of acid mine drainage, the water to be treated contains significant quantities of dissolved iron and aluminum. These materials will react as calcium sulfate scavengers if the raw water is treated with lime in the pH 11.9 to 12.0 range. Thus, acid mine drainage contains materials which can be used to remove sulfate from the water without addition of sodium aluminate. In general, however, the dissolved iron and aluminum contents of the raw AMD are insufficient to reduce sulfate levels to 250 mg/liter, the maximum concentration permitted under drinking water standards.

The form of calcium sulfoaluminates and sulfoferrites produced when the alumina-lime-soda process is used for treating acid mine drainage appears to be a mixture of the high-sulfate and low-sulfate forms, with the latter species predominating. This observation is contrary to those observed when the alumina-lime-soda process is applied to brackish waters having calcium/magnesium sulfate salinity,[1/] and which contain no dissolved iron or aluminum. In the OSW study, the calcium sulfoaluminate composition corresponded almost totally with the high-sulfate form, i.e., 3 moles of calcium sulfate removed per mole of Al_2O_3. The principal difference between the OSW work and the present study dealing with acid mine drainage lies in the iron content in raw water. Virtually no iron was present in raw water used in the former study, while iron concentrations were in the 20 to 100 ppm range for the present study.

We believe that the reason for the low-sulfate form is due to part of the aluminum (from *in situ* aluminum or sodium aluminate) becoming "encapsulated" by calcium sulfoferrite from the *in situ* iron. This encapsulation would make some of the aluminum unavailable for reaction with calcium sulfate to form ettringite.

SECTION VII

ALUMINA-LIME-SODA PROCESS CHEMISTRY FOR RECOVERING WATER FROM ACID MINE DRAINAGE

The alumina-lime-soda process involves two stages as described earlier in Section IV. This section will describe in detail the several chemical reactions which occur in the two process stages. The description is based upon experimental results attained with the Proctor No. 2 acid mine drainage. In addition, formulae for estimating quantities of the treatment chemicals will be presented.

STAGE I - AMD REACTIONS WITH LIME AND SODIUM ALUMINATE

There are four basic reactions which occur in Stage I: neutralization of acid; precipitation of metals; removal of sulfate by *in situ* iron and aluminum; and removal of sulfate by sodium aluminate.

Neutralization of Acid

The first reaction that occurs when lime and sodium aluminate are added to raw AMD is the neutralization of acid. This neutralization is simply:

$$H^+ + OH^- \longrightarrow H_2O \qquad (7\text{-}1)$$

Some of the acid is due to the hydrolysis of dissolved iron and aluminum sulfates in the AMD.

$$Fe^{+++} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+ \qquad (7\text{-}2)$$

$$Al^{+++} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+ \qquad (7\text{-}3)$$

When lime is added, the acid from the hydrolysis is neutralized, and iron and aluminum precipitate as their respective hydroxides.

$$Fe^{+++} + 3OH^- \longrightarrow Fe(OH)_3 \qquad (7\text{-}4)$$

$$Al^{+++} + 3OH^- \longrightarrow Al(OH)_3 \qquad (7\text{-}5)$$

Precipitation of Metals

In general, only the trivalent metals will be precipitated during the neutralization reactions, i.e., raising the pH to the neutral (pH = 7.0) range. When the pH is raised to 12.0, all metals in the raw AMD, with the exception of the alkali metals (sodium and potassium) and calcium, will precipitate. Common metals in mine drainage include magnesium, manganese, and ferrous iron. The precipitation reactions are:

$$Mg^{++} + 2OH^{-} \longrightarrow Mg(OH)_2 \qquad (7\text{-}6)$$

$$Mn^{++} + 2OH^{-} \longrightarrow Mn(OH)_2 \qquad (7\text{-}7)$$

$$Fe^{++} + 2OH^{-} \qquad Fe(OH)_2 \qquad (7\text{-}8)$$

As the pH is raised, the ferrous iron and manganous hydroxides will rapidly oxidize to their respective trivalent hydroxides.

$$2Fe(OH)_2 + 1/2O_2 + H_2O \longrightarrow 2Fe(OH)_3 \qquad (7\text{-}9)$$

$$2Mn(OH)_2 + 1/2O_2 \longrightarrow 2MnO(OH) + H_2O \qquad (7\text{-}10)$$

Thus, the alumina-lime-soda process overcomes problems associated with oxidation of ferrous and manganous components normally encountered in conventional neutralization processes where pH is raised only near neutrality.

Removal of Sulfate with *in situ* Iron and Aluminum

The key reaction in the alumina-lime-soda process involves the removal of calcium sulfate by aluminate ion at a system pH of 12.0. Results of the present study indicate that the iron and aluminum components of the raw AMD will remove some calcium sulfate in the Stage I reactions. Products generated by the *in situ* iron and aluminum appear to approximate the low-sulfate form of calcium sulfoaluminate and calcium sulfoferrite. (A discussion of the low-sulfate and high-sulfate sulfoaluminates and sulfoferrites is presented in Section VI.) Reactions of *in situ* iron and aluminum thus can be represented:

$$2Fe(OH)_3 + 4Ca^{++} + SO_4^{=} + 6OH^{-} \longrightarrow CaSO_4 \cdot Fe_2O_3 \cdot 3CaO \cdot xH_2O \qquad (7\text{-}11)$$

$$2Al(OH)_3 + 4Ca^{++} + SO_4^{=} + 6OH^{-} \longrightarrow CaSO_4 \cdot Al_2O_3 \cdot 3CaO \cdot xH_2O \qquad (7\text{-}12)$$

Methods for estimating the amount of sulfate that is removed by the in situ iron and aluminum are discussed later in this section and in Appendix B.

Removal of Sulfate by Sodium Aluminate

Normally, there is insufficient iron and aluminum content in acid mine drainage to reduce sulfate to acceptable levels. In order to increase the sulfate removal of the process, sodium aluminate is added to the system to further reduce the sulfate concentration.

When sodium aluminate is added, each mole of alumina will remove 1 mole of sulfate. The reaction may be generalized as:

$$4(Na^{+}AlO_2^{-}) + 9Ca^{++} + 4SO_4^{=} + 8OH^{-} \longrightarrow 4CaSO_4 \cdot 2Al_2O_3 \cdot 5CaO \cdot Na_2O \cdot xH_2O + 2Na^{+} \qquad (7\text{-}13)$$

The experimental results indicate that calcium oxide is removed along with calcium sulfate in the calcium sulfoaluminates (and sulfoferrites) formed by sodium aluminate and by in situ iron and aluminum. This lime is an essential part of the calcium sulfosalts, and is needed to keep the removed calcium sulfate from resolubilizing in the process. In the sodium aluminate experiments, we found that sodium oxide, Na_2O, is also being removed. Thus, we show 1 mole of Na_2O removed with each 4 moles of $CaSO_4$, 2 moles of Al_2O_3, and 5 moles of CaO in Eq. (7-13). However, the data further indicate that the exact amount of Na_2O removed is highly variable. Therefore, a more proper representation of the composition of solids removed by sodium aluminate is:

$$4CaSO_4 \cdot 2Al_2O_3 \cdot 6(CaO,\ Na_2O) \cdot xH_2O \qquad (7\text{-}14)$$

In this representation, the variability of sodium oxide to aluminum ratio can be accounted for.

The composition (7-14) represents a mixture of the high-sulfate and low-sulfate forms of calcium sulfoaluminate in a 50:50 mixture.

$$4CaSO_4 \cdot 2Al_2O_3 \cdot 6(CaO,\ Na_2O) \cdot xH_2O \longrightarrow CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O) \cdot xH_2O + 3CaSO_4 \cdot Al_2O_3 \cdot 3(CaO,\ Na_2O) \cdot xH_2O \qquad (7\text{-}15)$$

Note that the first product has the same composition of that generated from the in situ aluminum, the low-sulfate calcium sulfoaluminate. The second product contains 3 moles of sulfate for every mole of Al_2O_3 (high-sulfate form), and has a composition similar to that of ettringite, the calcium sulfoaluminate responsible for controlling set in portland cement hardening.

STAGE II - CARBONATION

The second stage of the alumina-lime-soda process involves the addition of carbon dioxide to reduce pH to acceptable levels. The carbonation step also removes hardness since calcium carbonate is precipitated in the reaction. The basic chemical reaction in Stage II is:

$$2OH^- + Ca^{++} + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (7\text{-}16)$$

In the actual process, effluent from Stage I is mixed with raw mine drainage. As has been discussed in Section V, the sulfate levels from Stage I are about 100 mg/liter, and causticity levels are about 600 mg/liter as $CaCO_3$. Thus, sulfate concentrations in product water can be increased to higher levels. (Sulfate concentrations of 250 mg/liter are permitted under U.S. Public Health Service Standards.) As a result, raw AMD can be used to neutralize a part of the excess causticity and increase sulfate levels to 250 mg/liter. The partial neutralization of Stage I effluent involves the neutralization of reactions, (7-1), (7-2), and (7-3), discussed earlier and lessens the amount of carbon dioxide needed for complete neutralization.

The optimum pH for precipitating the most hardness from an alkaline solution is 10.3. At this pH, hardness is in the form of calcium carbonate at a 35 mg/liter concentration. If excess CO_2 is added to drop the pH to lower values, the precipitated calcium carbonate will redissolve forming calcium bicarbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{++} + 2HCO_3^- \qquad (7\text{-}17)$$

The presence of calcium bicarbonate will result in a harder product water than need be, as well as unnecessary consumption of carbon dioxide.

However, if the precipitated calcium carbonate is removed while the pH is at 10.3, the subsequent addition of CO_2 will drop the pH to the 7.0 to 7.5 range. Since only 35 mg/liter of calcium carbonate is present in solution after separation, the amount of carbon dioxide needed to convert dissolved carbonate to bicarbonate for dropping the pH is minimized.

$$CO_3^{=} + CO_2 + H_2O \longrightarrow 2HCO_3^{-} \qquad (7\text{-}18)$$

Thus, we have included in the process design provisions for carbonating Stage II effluent after its separation from calcium carbonate in order to obtain product water meeting pH specifications.

CHEMICAL REQUIREMENTS FOR THE ALUMINA-LIME-SODA PROCESS

The preceding discussion of alumina-lime-soda chemistry has served as the basis for the development of formulae for estimating chemical requirements for the process. Details of the mathematical development of the formulae are presented in Appendix B. The formulae have been developed on the basis of two sodium aluminates. The first is referred to as "Dry-$NaAlO_2$" and is solid sodium aluminate now commercially available. The second is "Calcined" (Cal-$NaAlO_2$) and represents sodium aluminate produced by calcining a mixture of soda ash and bauxite. The production of Cal-$NaAlO_2$ is discussed in Section IX of the report.

The formulae for estimating chemical requirements for Stage I of the alumina-lime-soda process are:

Sodium Aluminate:

$$g\text{Dry-}NaAlO_2/\ell = \frac{R_{SO_4} - E_{SO_4} - 0.86Fe - 1.78Al}{809} \qquad (7\text{-}19)$$

$$g\text{Cal-}NaAlO_2/\ell = \frac{R_{SO_4} - E_{SO_4} - 0.86Fe - 1.78Al}{998} \qquad (7\text{-}20)$$

where R_{SO_4} = sulfate concentration in raw AMD, mg/ℓ

E_{SO_4} = sulfate concentration in effluent from Stage I, $\geq$ 100 mg/ℓ

Fe = total iron concentration in raw AMD (*in situ* iron), mg/ℓ

Al = aluminum concentration in raw AMD (*in situ* aluminum), mg/ℓ

Hydrated Lime, 93%:

$$gCaO/\ell:(Dry\text{-}NaAlO_2) = \left[0.00079\ acid + 0.00332\ Mg + 0.00145\ Mn + 0.00213\ Fe + 0.00442\ Al + 0.477\right] + 0.621\ (gDry\text{-}NaAlO_2/\ell) \quad (7\text{-}21)$$

$$gCaO/\ell:(Cal\text{-}NaAlO_2) = \left[0.00079\ acid + 0.00332\ Mg + 0.00145\ Mn + 0.00213\ Fe + 0.00442\ Al + 0.477\right] + 0.739\ (gCal\text{-}NaAlO_2/\ell) \quad (7\text{-}22)$$

where acid = acidity of raw AMD, mg/ℓ as $CaCO_3$

Mg = magnesium concentration in raw AMD, mg/ℓ

Mn = manganese concentration in raw AMD, mg/ℓ

Fe = total *in situ* iron in raw AMD, mg/ℓ

Al = total *in situ* aluminum in raw AMD, mg/ℓ

$Dry\text{-}NaAlO_2$ = dosage of dry sodium aluminate, g/ℓ

$Cal\text{-}NaAlO_2$ = dosage of calcined sodium aluminate, g/ℓ

The choice of the formulae used depends upon the kind of sodium aluminate used in Stage I. The formulae will yield dosages in grams per liter which is equivalent to kilograms per 1,000 liters for full-scale systems. Dosages calculated with the formulae can be converted to English units (pounds per 1,000 gal) by multiplying results by 8.34.

STAGE II - RATIO MIXING OF STAGE I EFFLUENT/RAW AMD AND CARBONATION

The formula for estimating carbon dioxide requirements in Stage II of the process does not depend upon sodium aluminate type. Rather,

it depends upon the causticity of the blend of Stage I effluent and raw AMD for produce water having the desired sulfate concentration. In establishing carbon dioxide requirements, one must also determine the proportions of Stage I effluent and raw AMD in the blend.

Carbon Dioxide:

$$gCO_2/\ell = 0.00046 \left[CAUS + 35\right] \qquad (7\text{-}23)$$

where CAUS = causticity of the blend of Stage I effluent and raw AMD, mg/ℓ as $CaCO_3$

The causticity (CAUS) is the difference between the hydroxide alkalinity of Stage I effluent and the acidity of raw AMD. The additional 35 mg/liter requirement in the formula represents that CO_2 which is used to drop the pH from 10.3 to the 7.0 to 8.0 range.

$$CAUS = EFF \times 600 - AMD \times acid \qquad (7\text{-}24)$$

where EEF = fraction of the blend that is Stage I effluent

AMD = 1 - EEF = fraction of blend that is raw AMD

acid = acidity of raw AMD, mg/ℓ as $CaCO_3$

600 = hydroxide alkalinity of Stage I effluent, mg/ℓ as $CaCO_3$

The fraction of the blend which is Stage I effluent is determined on the basis of sulfate values in the raw AMD, in the Stage I effluent, and in the finished product water. This term is calculated as follows:

$$EFF = \frac{R_{SO_4} - I_{SO_4}}{R_{SO_4} - E_{SO_4}} \qquad (7\text{-}25)$$

where R_{SO_4} = sulfate concentration in raw AMD, mg/ℓ

P_{SO_4} = sulfate concentration in finished product water, usually 250 m/ℓ

E_{SO_4} = sulfate concentration in Stage I effluent, ≥ 100 mg/ℓ

SECTION VIII

CHEMICAL COSTS FOR THE ALUMINA-LIME-SODA PROCESS FOR SEVERAL ACID MINE DRAINAGES IN PENNSYLVANIA

Principles of the alumina-lime-soda process have been applied to several acid mine drainages in Pennsylvania. Chemical compositions of the raw AMD were used in conjunction with formulae developed for estimating chemical requirements discussed previously. Results of this exercise are presented in Tables 9 through 14.

Also included in Tables 9 through 14 are estimated chemical costs for treating the various raw mine drainages to sulfate levels of 250 mg/liter. The costs are based on two kinds of sodium aluminate--"dry" sodium aluminate which is available commercially, and "calcined" sodium aluminate which is manufactured by heating a soda ash-bauxite mixture to 1000°C (1832°F). Dry sodium aluminate contains water of crystallization and hence contains less active alumina than does calcined. A discussion of the two kinds of sodium aluminate is presented in Section IX. As can be seen from the tables, the use of the calcined sodium aluminate is preferred because of its lower cost.

The chemical costs have been calculated using the following bases:

Chemical	Cost ($/kg)	Cost ($/lb)
Dry sodium aluminate	0.298	0.135
Calcined sodium aluminate	0.176	0.080
Hydrated lime, 93%	0.044	0.020
Carbon dioxide	0.110	0.050

The cost for dry sodium aluminate is that quoted by Reynolds Metals Company for bulk purchases. The cost for calcined sodium aluminate is discussed in detail in Section IX. The costs of lime and carbon dioxide are estimated based upon current price ranges of the two chemicals.

Table 9. PROCTOR NO. 1, HOLLYWOOD, PENNSYLVANIA, RAW AMD TREATED BY ALUMINA-LIME-SODA: 25% TREATED IN STAGE 1

	Before treatment[a/]	After treatment
pH	3.8	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	180	0
Sulfate, mg/ℓ as SO_4	300	250
Chloride, mg/ℓ as Cl	Unknown	Unknown
Bicarbonate, mg/ℓ as $CaCO_3$	0	35
Calcium, mg/ℓ as Ca	6	58
Magnesium, mg/ℓ as Mg	15	14
Sodium, mg/ℓ as Na	8	20
Iron, mg/ℓ as Fe	30	nil
Aluminum, mg/ℓ as Al	20	nil
Manganese, mg/ℓ as Mn	Unknown	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.02	0.003	0.02	0.003
Sodium aluminate	0.04	0.012	0.04	0.006
Hydrated lime, 93% $Ca(OH)_2$	0.24	0.011	0.24	0.011
Total chemical costs ($/1,000 cu m)		0.026		0.020
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$1,000 gal
Carbon dioxide	0.20	0.010	0.20	0.010
Sodium aluminate	0.37	0.050	0.30	0.024
Hydrated lime 93% $Ca(OH)_2$	2.03	0.041	2.02	0.040
Total chemical costs ($/1,000 gal)		0.101		0.074

a/ Raw AMD data from present study.

Table 10. COMMONWEALTH OF PENNSYLVANIA HAWK RUN AMD PLANT
PHILIPSBURG, PENNSYLVANIA
RAW AMD TREATED BY ALUMINA-LIME-SODA: 75%
TREATED IN STAGE I

	Before treatment[a/]	After treatment
pH	3.7	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	384	0.00
Sulfate, mg/ℓ as SO_4	648	250
Chloride, mg/ℓ as Cl	Unknown	Unknown
Bicarbonate, mg/ℓ as $CaCO_3$	0.00	35
Calcium, mg/ℓ as Ca	118	20
Magnesium, mg/ℓ as Mg	24	10
Sodium, mg/ℓ as Na	Unknown	150
Iron, mg/ℓ as Fe	101	nil
Aluminum, mg/ℓ as Al	Unknown	nil
Manganese, mg/ℓ as Mn	Unknown	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.18	0.02	0.18	0.02
Sodium aluminate	0.45	0.13	0.36	0.06
Hydrated lime, 93% $Ca(OH)_2$	1.13	0.05	1.12	0.05
Total chemical cost ($/cu m)		0.20		0.13
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$/1,000 gal
Carbon dioxide	1.54	0.08	1.54	0.08
Sodium aluminate	3.74	0.50	3.03	0.24
Hydrated lime, 93% $Ca(OH)_2$	9.38	0.19	9.30	0.19
Total chemical cost ($/1,000 gal)		0.77		0.51

a/ Raw water data from: R. Kunin and J. J. Demchalk, "The Use of Amberlite Ion Exchange Resins in Treating Acid Mine Waters at Philipsburg, Pennsylvania," Paper presented at fifth Symposium in Coal Drainage Research, Louisville, Kentucky, October 1974.

Table 11. PROCTOR NO. 2, HOLLYWOOD, PENNSYLVANIA
RAW AMD TREATED BY ALUMINA-LIME-SODA: 80%
TREATED IN STAGE I

	Before treatment[a]	After treatment
pH	2.8	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	700	0
Sulfate, mg/ℓ as SO_4	750	250
Chloride, mg/ℓ as Cl	Unknown	Unknown
Bicarbonate, mg/ℓ as $CaCO_3$	0	35
Calcium, mg/ℓ as Ca	8	20
Magnesium, mg/ℓ as Mg	25	10
Sodium, mg/ℓ as Na	2	145
Iron, mg/ℓ as Fe	100	nil
Aluminum, mg/ℓ as Al	40	nil
Manganese, mg/ℓ as Mn	Unknown	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.18	0.02	0.18	0.02
Sodium aluminate	0.51	0.15	0.41	0.07
Hydrated lime, 93% $Ca(OH)_2$	1.58	0.07	1.56	0.07
Total chemical costs ($/cu m)		0.24		0.16
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$/1,000 gal
Carbon dioxide	1.48	0.07	1.48	0.07
Sodium aluminate	4.26	0.58	3.46	0.28
Hydrated lime, 93% $Ca(OH)_2$	13.17	0.26	13.03	0.26
Total chemical costs ($/1,000 gal)		0.91		0.61

a/ Raw AMD data from present study.

Table 12. SAWMILL RUN, RAW AMD TREATED BY ALUMINA-LIME-SODA: 85% TREATED IN STAGE 1

	Before treatment[a/]	After treatment
pH	3.2	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	690	0
Sulfate, mg/ℓ as SO_4	1,020	250
Chloride, mg/ℓ as Cl	40	40
Bicarbonate, mg/ℓ as $CaCO_3$	0	35
Calcium, mg/ℓ as Ca	109	30
Magnesium, mg/ℓ as Mg	81	15
Sodium, mg/ℓ as Na	Unknown	270
Iron, mg/ℓ as Fe	28	nil
Aluminum, mg/ℓ as Al	8	nil
Manganese, mg/ℓ as Mn	5	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.21	0.02	0.21	0.02
Sodium aluminate	0.97	0.29	0.79	0.14
Hydrated lime, 93% $Ca(OH)_2$	1.85	0.08	1.83	0.08
Total chemical cost ($/cu m)		0.39		0.24
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$/1,000 gal
Carbon dioxide	1.74	0.09	1.74	0.09
Sodium aluminate	8.11	1.09	6.57	0.53
Hydrated lime, 93% $Ca(OH)_2$	15.40	0.31	15.22	0.30
Total chemical cost ($/1,000 gal)		1.49		0.92

a/ Raw AMD data from Commonwealth of Pennsylvania Department of Environmental Resources.

Table 13. YOUNG AND SON COAL CORPORATION, PARKER'S LANDING, PENNSYLVANIA
RAW AMD TREATED BY ALUMINA-LIME-SODA: 90%
TREATED IN STAGE I

	Before treatment[a/]	After treatment
pH	2.6	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	785	0
Sulfate, mg/ℓ as SO_4	1,360	250
Chloride, mg/ℓ as Cl	Unknown	Unknown
Bicarbonate, mg/ℓ as $CaCO_3$	0	35
Calcium, mg/ℓ as Ca	138	28
Magnesium, mg/ℓ as Mg	58	10
Sodium, mg/ℓ as Na	Unknown	300
Iron, mg/ℓ as Fe	225	nil
Aluminum, mg/ℓ as Al	38	nil
Manganese, mg/ℓ as Mn	4	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.24	0.03	0.24	0.03
Sodium aluminate	1.17	0.35	0.95	0.17
Hydrated lime, 93% $Ca(OH)_2$	0.24	0.03	0.24	0.03
Total chemical costs ($/cu m)		0.49		0.31
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$/1,000 gal
Carbon dioxide	1.96	0.10	1.96	0.10
Sodium aluminate	9.72	1.31	7.89	0.63
Hydrated lime, 93% $Ca(OH)_2$	21.35	0.43	21.13	0.42
Total chemical costs ($/1,000 gal)		1.84		1.15

a/ Raw AMD data from Commonwealth of Pennsylvania Department of Environmental Resources.

Table 14. BETHLEHEM MINES CORPORATION MARIANNA MINE NO. 58
MARIANNA, PENNSYLVANIA
RAW AMD TREATED BY ALUMINA-LIME-SODA: 100%
TREATED IN STAGE 1

	Before treatment[a/]	After treatment
pH	2.64	7.0-8.0
Acidity, mg/ℓ as $CaCO_3$	4,080	0
Sulfate, mg/ℓ as SO_4	10,000	250
Chloride, mg/ℓ as Cl	1,830	1,830
Bicarbonate, mg/ℓ as $CaCO_3$	0	35
Calcium, mg/ℓ as Ca	444	14
Magnesium, mg/ℓ as Mg	404	3
Sodium, mg/ℓ as Na	2,420	4,300
Iron, mg/ℓ as Fe	815	nil
Aluminum, mg/ℓ as Al	475	nil
Manganese, mg/ℓ as Mn	38	nil

	Commercial dry sodium aluminate		Calcined sodium aluminate	
	Quantity	Cost	Quantity	Cost
Chemical requirements (kg/cu m):	Kg	$/cu m	Kg	$/cu m
Carbon dioxide	0.3	0.03	0.3	0.03
Sodium aluminate	10.1	3.01	8.2	1.45
Hydrated lime, 93% $Ca(OH)_2$	15.2	0.67	15.0	0.66
Total chemical costs ($/cu m)		3.71		2.14
Chemical requirements (lb/1,000 gal):	Lb	$/1,000 gal	Lb	$/1,000 gal
Carbon dioxide	2.5	0.13	2.5	0.13
Sodium aluminate	84.5	11.41	68.5	5.48
Hydrated lime, 93% $Ca(OH)_2$	127.0	2.54	125.1	2.50
Total chemical costs ($/1,000 gal)		14.08		8.11

a/ Raw AMD data from Commonwealth of Pennsylvania, Department of Environmental Resources.

The keys to the costs of the alumina-lime-soda lie in two factors: the sulfate content of the raw mine drainage, which determines the fraction of mine drainage treated by alumina-lime-soda; and the amount of *in situ* iron and aluminum contained within the mine drainage. These two factors determine the quantity of sodium aluminate which is required for the process; and since sodium aluminate is the most expensive treatment chemical of the process, its requirement has the greatest effect on chemical costs.

It would appear from the data that sulfate concentrations in the 1,100- to 1,200-mg/liter range are a likely upper limit for utilizing the alumina-lime-soda process. In this range, about 85% of the raw AMD is treated by alumina-lime-soda, and overall chemical costs lie in the range of $0.25 to $0.30/cu m ($0.95 to $1.15/1,000 gal) of product water.

The chemical cost estimates in Tables 9 through 14 were made in the following manner. First, the fraction of Stage I effluent needed for the final blend was computed based on sulfate concentrations in raw AMD, sulfate in the blend at 250 mg/liter, and sulfate in the Stage I effluent of 100 mg/liter.

Second, sodium aluminate and lime dosages were determined using formulas as developed in Appendix B. These dosages were multiplied by the fraction treated and by the factor 1.05 to account for water losses in the Stage I sludges.

Third, the causticity of the blended Stage I effluent and raw AMD was calculated for the carbonation step. From this value, the requirement for carbon dioxide was estimated. The carbon dioxide requirement was multiplied by 1.03 to account for water losses in the Stage II $CaCO_3$ precipitate.

These estimates of treatment chemical quantities were then multiplied by the appropriate chemical cost and the results summed to yield the chemical cost values presented in Tables 9 through 14.

SECTION IX

SODIUM ALUMINATE FOR THE ALUMINA-LIME-SODA PROCESS

The key to alumina-lime-soda process economics lies in the cost of sodium aluminate. Sodium aluminate is a chemical which has limited application as a flocculating agent, and as a source of specialty alumina chemicals, e.g., catalysts. As a result, the demand for sodium aluminate has been somewhat limited. In 1972, the production of sodium aluminate was estimated to be about 16,400 metric tons (18,000 tons)/year.

The most recent price of dry sodium aluminate is $250.00/metric ton ($275.00/ton). This quote from Reynolds Metals Company on July 1, 1975, represents a bagged cost, and they will discount the price $4.55/metric ton ($5.00/ton) if shipped on a bulk basis. Thus, the current sodium aluminate price is $0.176/kg ($0.135/lb) on a bulk basis. Liquid sodium aluminate costs $0.194/kg ($0.088/lb) on an 18,000-kg (40,000-lb) basis (Nalco Chemical Company). When converted to a dry basis, the cost equivalent today of sodium aluminate is about $0.44/kg ($0.20/lb), rendering liquid sodium aluminate noncompetitive with the solid in full-scale plant operations. Thus, liquid sodium aluminate was not considered in cost estimations.

If a number of alumina-lime-soda plants using mine drainage with sulfate concentrations in the 1,100- to 1,200-mg/liter range totaling 19 million liters (5 million gallons) per day were built, one would need approximately 5,500 to 7,300 metric tons (6,000 to 8,000 tons) per year of dry sodium aluminate. If the alumina-lime-soda process was applied to areas having other kinds of problems, e.g., high calcium sulfate waters in the western states, the demand for sodium aluminate would increase further. This quantity represents about a 50% increase in the demand for the chemical. In addition, high grade sodium aluminate would not be required. Thus, it is likely that the price would drop substantially by the time the process is developed to full scale.

An alternative approach to sodium aluminate would be its manufacture by calcining bauxite and soda ash,[5] rather than by its crystallization from sodium aluminate solution. Process principles are almost identical with those associated with portland cement manufacture, except that the temperature of the rotary kiln is in the 900 to 1100°C (1650 to 2000°F) range rather than in the 1300 to 1500°C (2350 to 2700°F) range. Approximate composition range of sodium aluminate produced from calcining bauxite-soda ash mixtures will be: Na_2O, 37 to 40%; Al_2O_3, 52 to 54%; and SiO_2, 5 to 7%.

Sodium aluminate produced by the calcination of bauxite and soda ash would be less pure than that presently produced commercially. Bauxite contains silicious impurities which result in the formation of sodium silicate as well as sodium aluminate. However, the soda fraction of the sodium silicate is useful in the alumina-lime-soda process so its presence is not detrimental. The silica will be precipitated in the sludge and not appear in the product water. The important constituent in the product is the sodium aluminate, since the alumina fraction is all important for sulfate removal.

The calcining of sodium carbonate and bauxite is a straight line process closely resembling the manufacturing process for cement. The same general types of equipment used in cement manufacturing are needed for calcining soda ash and bauxite to yield sodium aluminate, carbon dioxide, and water. The general types of equipment are: crushing, grinding, rotary kiln, and conveying and handling.

A cost estimate for a new 18,200 metric ton (20,000 ton)/year sodium aluminate plant based on calcining of soda ash and bauxite was made using cost data from previous years converted to 1975 dollars by the use of Marshall and Stevens Equipment Cost Index and the Construction Cost Index.

The selling price of sodium aluminate (85% purity) is calculated to be $0.176/kg ($0.08/lb). This price compares to sodium aluminate produced as a specialty product (72% purity) of $0.298/kg ($0.135/lb).

The cost estimate is given in Table 15.

Table 15. COST ESTIMATE: 20,000 TONS PER YEAR SODIUM ALUMINATE MANUFACTURING PLANT (CALCINE PROCESS)

Capital costs	
Equipment delivery cost	$ 500,000
Installation (1.05)	525,000
Buildings	80,000
Land [16.2 hectares (40 acres)]	200,000
Subtotal	1,305,000
Contig. at 20%	261,000
	1,566,000
Operating capital	434,000
Total capital cost	$2,000,000
18,200 metric tons (20,000 tons)/year, 350-day operation, 59,687 kg/day (132,638 lb/day)	
Operating costs per day	
Raw materials and fuel	$ 4,933.38
Utilities	500.00
Labor - 5 men at $3.75/hr	462.85
Supervision	35.71
Maintenance at 20% equipment cost	277.77
Capital cost at 7%	400.00
Depreciation at 6% equipment	85.71
at 2% building	4.57
Overhead and payroll taxes at 11%	509.14
Selling and advertising	663.19
Taxes and insurance	636.66
Total operating cost	$ 8,568.98/day
Total sales [at $0.176/kg ($0.08/lb)]	$ 10,611.04/day
Gross profit	$ 2,042.06/day
Gross profit	$ 714,721.00/year

Calcined sodium aluminate can be manufactured by utilizing excess capacity of a portland cement plant. The equipment and personnel need for the production of sodium aluminate from calcination of soda ash and bauxite are the standard pieces of equipment used to manufacture cement. A cement manufacturer producing sodium aluminate in his plant could cut the cost below the calculated cost for a new plant.

Raw material and fuel costs are based on the following assumptions. The bauxite raw material is assumed to be high grade having an alumina content of 55% and a silica content of 7% or less. Sufficient soda ash is mixed with the bauxite to form both sodium aluminate and sodium silicate. We have estimated bauxite costs to be $33/metric ton ($30/ton) for the low-silica material; the cost of soda ash is estimated to be $55/metric ton ($50/ton). These cost estimates have been made from recent data from the U.S. Bureau of Mines and the Chemical Marketing Reporter. After the bauxite and soda ash are mixed, the feed is fired at about 1000°C in a rotary kiln. The carbon dioxide evolved during the reaction is collected for its use in the alumina-lime-soda process, or for its purification and resale.

Thus, we conclude that sodium aluminate produced by calcining bauxite and soda ash is the product which should be sought for the full-scale use of the alumina-lime-soda water treatment process. Impurities in the product will not interfere with the process, and it will be anhydrous. The anhydrous nature of the bauxite-soda ash process is an advantage since "dry" sodium aluminate currently distributed contains about 25 to 30% water of crystallization. The added alumina in the calcined product (52 to 54% compared to 42 to 43% in the crystallized product) means that less calcined sodium aluminate is needed compared to the dry sodium aluminate.

SECTION X

ALUMINA-LIME-SODA PROCESS ECONOMICS

This section presents estimates of construction and operational costs for treatment of AMD water using the alumina-lime-soda process. Raw AMD considered for this economic analysis was assumed to be equivalent to Proctor No. 2. Plant capacities selected for the development of the cost estimates are 0.5 MGD, 1.0 MGD, and 5.0 MGD.* Almost all treatment plants needed for AMD water treatment should fall within the 0.5 to 5.0 MGD range; therefore, the cost estimates should be representative.

The costs developed are based on incorporating the following unit operations in the alumina-lime-soda process:

* Pump station
* Chemical mix basin
* Reacting basin
* Settling basin
* Carbonating basin
* Final storage basin
* Chemical feed system (storage tanks and feeders)
* Vacuum filter

All basins were assumed to be constructed of reinforced concrete. Most mixers, scrapers, baffling and structural supports would consist of corrosion-resistant materials due to alkaline conditions expected throughout the treatment process. One of the major equipment costs is the vacuum filter to separate Stage 1 effluent from the calcium sulfoaluminate/sulfoferrite sludges. With these assumptions, the total estimated construction costs (1975) for three plants of

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* 1 MGD = 3,780.000 liter/day = 3.780 cu m/day.

differing capacity utilizing the alumina-lime-soda process are shown below.

Plant capacity (MGD)	Total construction costs
0.5	$ 352,000
1.0	$ 516,000
5.0	$1,382,000

These costs include contingencies (10%), but exclude engineering and legal costs. These costs are displayed graphically in Figure 11.

The operation and maintenance costs (excluding depreciation) for the three plant sizes are estimated below. Costs are given in $/1,000 gal. The chemical costs shown are based on treatment of Proctor No. 2 AMD.

	0.5 MGD	1.0 MGD	5.0 MGD
Power	0.06	0.04	0.02
Labor	0.26	0.16	0.05
Chemical	0.61	0.61	0.61
Sludge disposal	0.11	0.11	0.11
Total ($/1,000 gal)	1.04	0.92	0.79
($/cu m)	0.27	0.24	0.21
Annual costs	$189,800	$335,800	$1,441,800

Figure 12 gives the graphical representation of the operation and maintenance costs.

Sodium aluminate manufactured by calcining bauxite and soda ash is assumed in the chemical cost estimates. The cost of solids disposal is assumed to be $5.00/ton of material having a dry solids content of 10%.

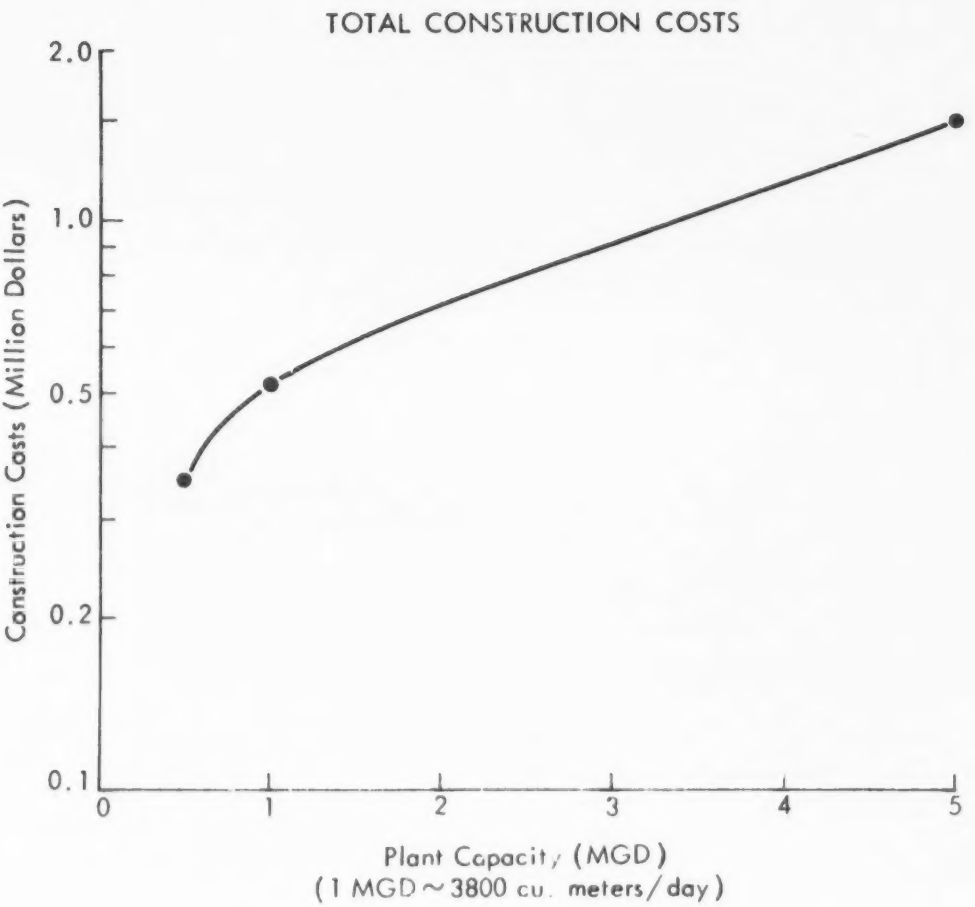


Figure 11. Total construction costs.

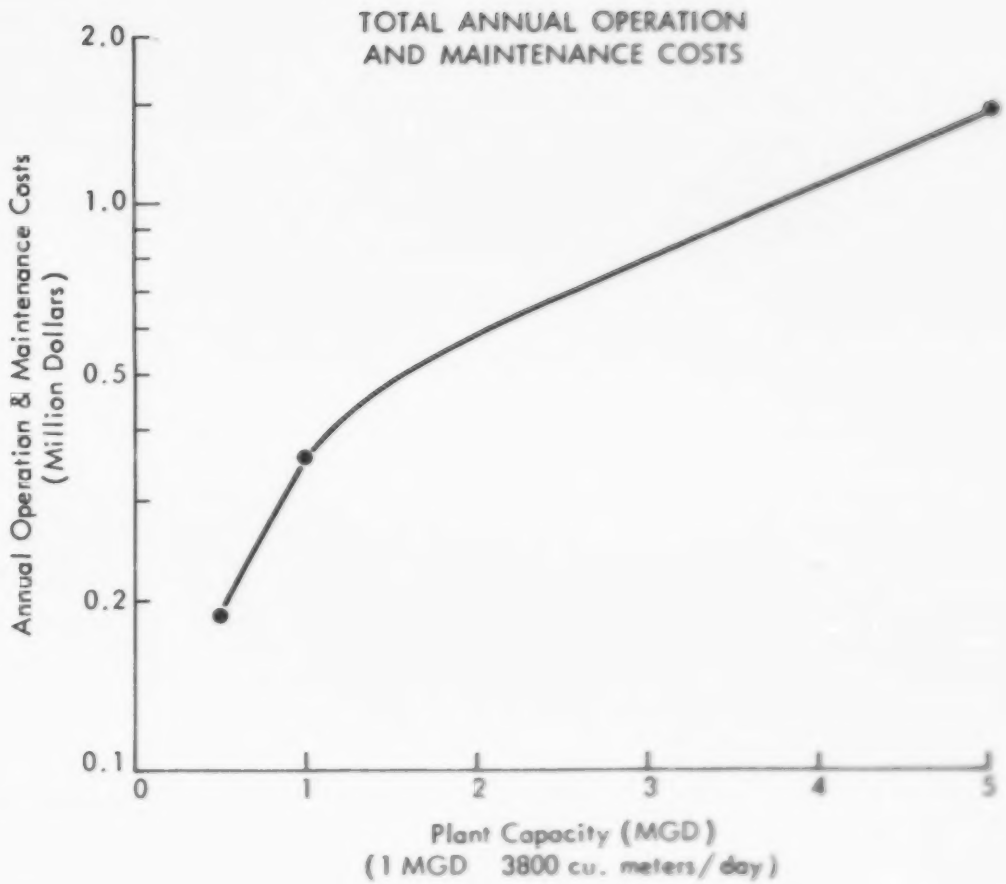


Figure 12. Total annual operation and maintenance costs.

SECTION XI

DISCUSSION OF RESULTS

The field studies conducted at the Hollywood facility resulted in an accumulation of about 800 hr of operating experience with the field unit. This experience amply demonstrated the basic operability of the alumina-lime-soda process in acid mine drainage, yielded the information and data needed to fully describe the process in terms of mine drainage, and firmed up various operating parameters needed to design a Phase II demonstration plant. The study also yielded information which permitted the assessment of costs of treating acid mine drainage with the alumina-lime-soda process and generally compared this process with other processes which are either in use or under investigation for mine drainage treatment.

The data accumulated during the program have demonstrated that the alumina-lime-soda process will produce water meeting drinking water standards from acid mine drainage. It is particularly useful for mine drainages having sulfate concentrations in the 400 mg/liter to 1,200 mg/liter range. Above 1,200 mg/liter, alumina-lime-soda costs become excessive because of increased treatment-chemical consumption and because of the larger quantity of water which must be treated in the first stage of the process. Below 400 mg/liter, raw mine drainage can be treated with lime to produce water suitable for many uses, and almost suitable as drinking water.

The alumina-lime-soda process is particularly attractive when compared to other water recovery processes, e.g., ion exchange or reverse osmosis. Alumina-lime-soda desalting depends strictly upon chemical processes and thus can be operated using conventional equipment and procedures. There are no resins to backwash or regenerate, nor are there chemicals to be processed and recycled as is found to be the case with ion exchange. There are no membranes to foul, nor is pretreatment of the water required as is the case with reverse osmosis. In the alumina-lime-soda process, removed constituents are found in easily dewatered sludge and are in a readily disposable form. There are no waste liquid streams needing treatment for disposal.

Scaling was not a serious problem in the alumina-lime-soda process during the Hollywood tests. During the course of the study (about 800 hr of operating experience), we did not observe any significant scaling of stirrers or reaction vessels, nor clogging of pipes or pumps. The precipitates formed during the process act as seeds for the reaction products, thus discouraging scale formation.

Since Stage I of the process operates under alkaline conditions (pH of 12.0), the reduced forms of dissolved iron and manganese are rapidly oxidized in the process. This feature ensures essentially complete removal of heavy metals which may be present in the raw acid mine drainage.

Analysis and interpretation of experimental data pertaining to process reactions have resulted in development of a good scientific rationale for reactions and products. This rationale will be generally applicable to mine drainage and has been organized to facilitate calculations of chemical and mass balances in mine drainage in general. The iron and aluminum present in raw mine drainage participate in alumina-lime-soda reactions to precipitate calcium sulfate and therefore serve a useful purpose in the process. Each mole of iron or aluminum present in the raw water will remove about one-half mole of sulfate as calcium sulfoferrite or sulfoaluminate. The rate of removal by aluminum is somewhat smaller than expected, possibly due to iron encapsulation of the aluminum. Aluminum added to the process as sodium aluminate, on the other hand, removes sulfate at a full sulfate/aluminum molar ratio. Hence, sodium aluminate is more effective than the in situ aluminum in raw acid mine drainage towards the removal of sulfate.

furnish sodium aluminate at a price considerably better than that currently quoted by manufacturers of Bayer-process alumina products.

The process consists of calcining high grade bauxite and soda ash. Experimental results suggest that a high purity sodium aluminate is unnecessary for the successful utilization of the alumina-lime-soda process. About 50 years ago, an accepted method for manufacturing sodium aluminate was the calcination of bauxite-soda ash mixtures. This method fell from favor because of silica impurities in the product. For the alumina-lime-soda process, however, the silica impurities are not deleterious, and sodium aluminate manufactured by the calcination process is recommended. The cost of sodium aluminate manufactured by calcining bauxite and soda ash is estimated to be about $0.176/kg ($0.08/lb), compared to $0.298/kg ($0.135/lb) for the dry sodium aluminate currently being marketed.

The process which evolved out of the field studies at the Hollywood mine drainage facility involves two stages. In Stage I, a majority of the input mine drainage is reacted with lime/sodium aluminate in a stirred reactor at a pH of 12.0. This system yields a precipitate of calcium sulfoaluminates and calcium sulfoferrites which is permitted to settle. The supernatant liquid is transferred to Stage II of the process; the settled sludge is filtered on a sand filter, and the filtrate recombined with the supernatant liquid. In Stage II of the process, the filtrate plus supernatant liquid is combined with the remaining fraction of the mine drainage in a reactor which completes the overall process as follows: the acid in the mine drainage is neutralized with excess alkalinity in the Stage I effluent; metal oxides and hydroxides are precipitated from the mine drainage; and carbon dioxide is added in sufficient quantities to reduce the pH to 10.3 and precipitate calcium carbonate. The liquid is then filtered to yield a second sludge plus an effluent which is lightly carbonated to a pH of 7 to 8. The relative proportions of mine drainage admitted to Stages I and II of the process are determined by the desired sulfate levels in the product water. For Project No. 2 mine drainage at the Hollywood facility, approximately three-fourths is treated in Stage I and the remaining one-fourth is added to Stage II to yield product water having sulfate concentrations of 250 mg/L or less. This method of operating the process maximizes the requirements for all the treatment chemicals--lime, sodium aluminate,

and carbon dioxide, and thus minimizes the costs for operating the process.

The alumina-lime-soda process uses the same principles as conventional waterworks processes using lime-soda ash softening. The principal difference between the two processes is that alumina-lime-soda operates at a pH of 12.0 rather than the 9.5 to 10.3 range in lime-soda ash softening. The similarity in the water treatment processes will result in utilization of standard water treatment-type equipment for the alumina-lime-soda process. As a consequence, capital and operating costs for alumina-lime-soda will be similar to those associated with conventional lime-soda ash treatment.

Costs of chemicals for treating various acid mine wastes by the alumina-lime-soda process have been calculated. Comparison of these costs plus estimated operating costs indicate that the alumina-lime-soda process is quite competitive with other processes which are being considered for mine drainage treatment. The Proctor No. 2 water (acidity of 700 mg/liter, sulfate of 750 mg/liter) is representative of mine drainages which are candidates for treatment by the alumina-lime-soda process. The cost for chemicals for Proctor No. 2 water is estimated to be $0.10/cm^3 ($0.4/1,000 gal).

The operation and maintenance costs for recovering water from Proctor No. 2 AMD have been estimated for plants having capacity of 1,900 cm^3/day (0.5 MGD); 3,800 cm^3/day (1.0 MGD) and 19,000 cm^3/day (5.0 MGD). The respective water recovery costs are: $0.27/cm^3 ($1.04/1,000 gal), $0.24/cm^3 ($0.92;1,000 gal), and $0.21/cm^3 ($0.79/1,000 gal).

A design for a 90,000 liter per day (50,000 gal/day) demonstration plant has been developed and is presented in this report. The estimated cost for procuring and constructing this plant is $95,000 to $100,000. Operation of such a plant for a period of 1 year is recommended to further demonstrate the process and obtain operating and cost information suitable for design of full-scale plants.

In summary:

The alumina-lime-soda process operated well on two mine drainages of moderate acidity and will yield water of drinking water quality.

The process requires only conventional water treatment equipment and thus will be easy to adapt to large scale. Operation will require no special skills not presently found in municipal water treatment practice.

Water yields are essentially quantitative, with no brines for disposal or recycle streams needing recovery. By-product sludges are similar to water treatment sludges.

Detailed engineering design data for bulk scale plants (up to about 5 MGD for acid mine drainage) are presently lacking. A pilot plant sized at about 190,000 liter per day (50,000 gal/day) is suitable for obtaining detailed engineering specifications and firming up cost data for construction and operation of bulk scale plants.

APPENDIX A

SPECIFICATIONS FOR THE 190,000 LITER/DAY (50,000 GAL/DAY) DEMONSTRATION PLANT

SYSTEMS DESIGN

The demonstration plant design is based on analytical results from laboratory tests and material balances based on the production of 190,000 liters/day (50,000 gal/day) of potable water. A flow sheet showing the system configuration is presented in Figure 13. The spatial layout of the plant is shown in Figure 14. The proposed continuous system features a chemical reactor, settler, carbonator, and sand filters. The chemical reactor is a continuous stirred tank reactor in which the lime and sodium aluminate are mixed and reacted with the AMD water. The pH in the reactor is maintained between 11.9 and 12.1 by lime addition. The settler and primary sand filter are solids separation units for removal of the suspended solids formed in the reactor. The carbonator is also a continuously stirred tank where the pH and sulfate concentration are adjusted by carbon dioxide addition and blending untreated AMD water with clarified settler--primary filter effluent. A final sand filter is needed for removal of residual solids formed in the carbonator.

The material balances were solved to determine the flow rates through each segment of the system. The following material balances were used to determine component flow rates, X_i, in the system depicted in Figure 15.

where X_i = water flow rate

a = solids weight fraction

b = sulfate weight fraction

Water Balances

overall: $X_1 = X_2 + X_{11} + 50{,}000$

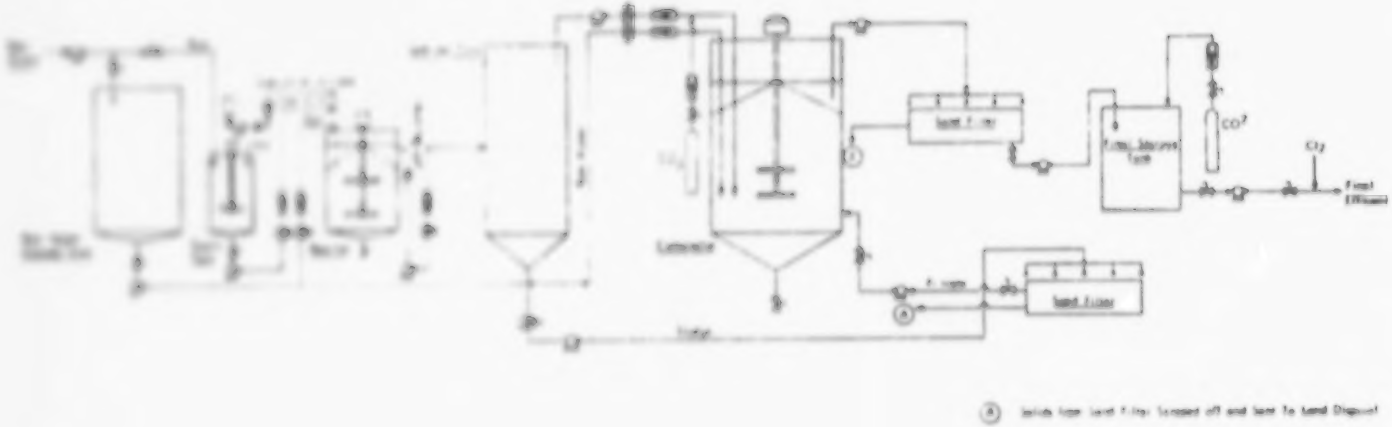


Figure 13. System configuration for the 190,000 liter/day (50,000 gal/day) demonstration plant.

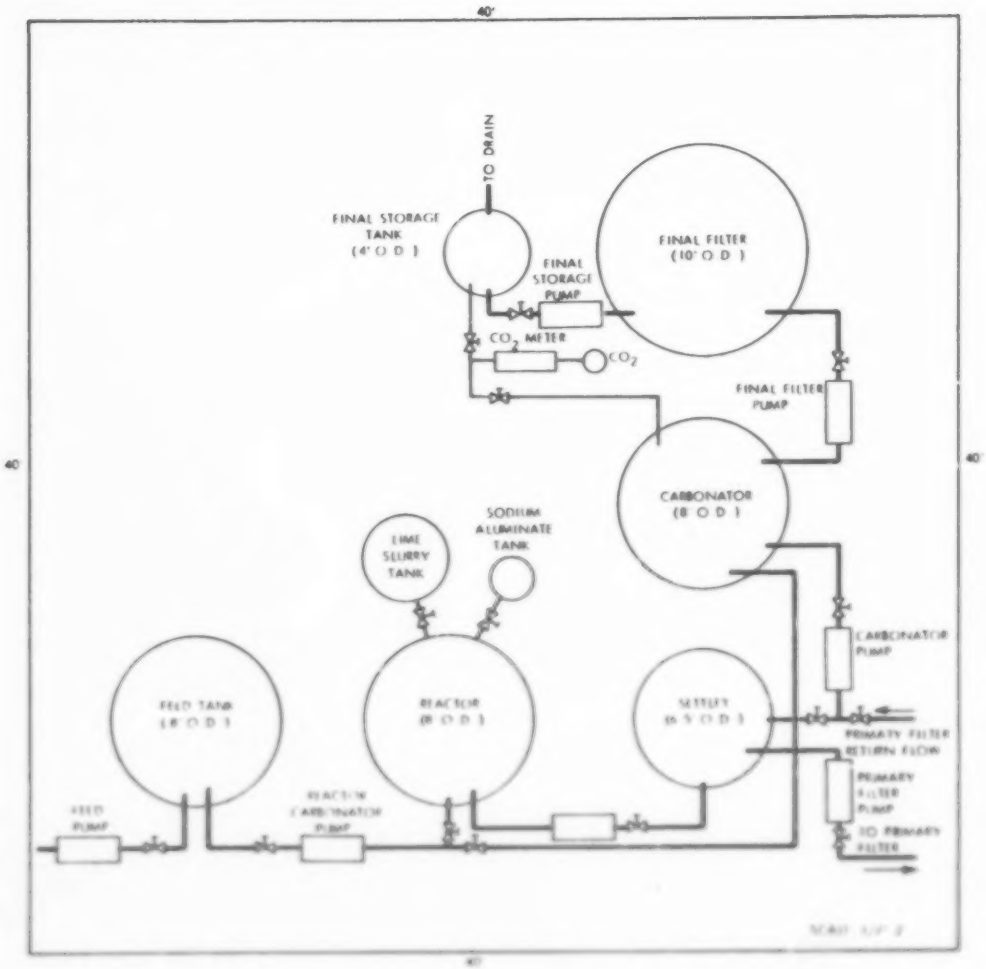
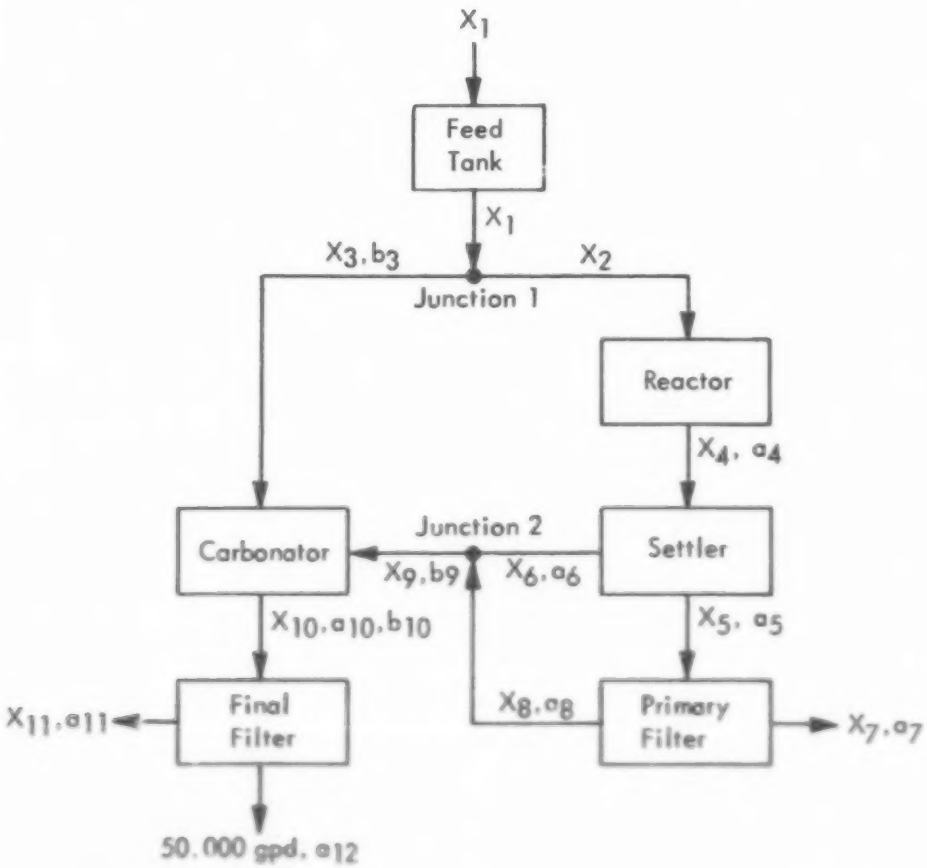


Figure 14. Spatial layout of the 190,000 liter/day (50,000 gal/day) demonstration plant.



Xi = Water Flow Rate (gpd)
ai = Solids Weight Fraction
bi = Sulfate Weight Fraction

Figure 15. Flow diagram to determine material balance.

Junction 1: $X_1 = X_2 + X_3$

Settler: $X_4 = X_5 + X_6$

Primary filter: $X_5 = X_7 + X_8$

Junction 2: $X_9 = X_6 + X_8$

Carbonator: $X_{10} = X_3 + X_9$

Final filter: $X_{10} = X_{11} + 50{,}000$

Solids Balances

Settler: $a_4X_4 = a_5X_5 + a_6X_6$

Primary filter: $a_5X_5 = a_7X_7 + a_8X_8$

Final filter: $a_{10}X_{10} = a_{11}X_{11} + a_{12}50{,}000$

Sulfate Balance

Carbonator: $b_{10}X_{10} = b_3X_3 + b_9X_9$

The equations can be combined algebraically to yield the following expressions for calculation of flow rates, X_i, in the system.

$$X_2 = 50{,}000/\left[(1 - K_3)(1 - K_1K_2)(1 + K_4)\right]$$

where $K_1 = (a_4 - a_6)/(a_5 - a_6)$

$K_2 = (a_5 - a_8)/(a_7 - a_8)$

$K_3 = (a_{10} - a_{12})/(a_{11} - a_{12})$

$K_4 = (b_{10} - b_9)/(b_3 - b_{10})$

$K_5 = K_1K_2$

$K_6 = (1 - K_1)K_2$

$K_7 = K_2K_5$

$K_8 = (1 - K_2)K_5$

$K_9 = K_6 + K_8$

The final filtration values for a_{11} and a_{12} were estimated as 0.05 and 0.0, respectively.

$a_4 = 0.0060$ $\quad$ $a_8 = 0.0$

$a_5 = 0.0190$ $\quad$ $a_{10} = 0.0005$

$a_6 = 0.0002$ $\quad$ $a_{11} = 0.05$

$a_7 = 0.10$ $\quad$ $a_{12} = 0.0$

The b_3 value used for design was 0.00075 (750 ppm), which is the sulfate concentration of Proctor No. 2 AMD water.

$$X_3 = K_4 X_9$$

$$X_{10} = X_3 + X_1$$

$$X_{11} = K_3 X_{10}$$

The K_1, K_2 and K_3 factors were calculated using solids concentration data from settling and filtration tests conducted in the laboratory. It is notable that the K factors are dependent on concentration only and independent of flow. K_1 can be calculated from experimental settling data, while K_2 and K_3 are calculated from filtration data.

K_4 is the ratio of the flow rates of streams X_3 to X_9 as they enter the carbonator. The two streams are mixed to adjust the pH and sulfate concentration. For design purposes the drinking water standard of 250 ppm (wt. fraction = 0.00025) was selected as the sulfate concentration in the carbonator effluent. Laboratory results indicate that the reactor should be operated to maintain a 100 ppm (wt. fraction = 0.0000) residual sulfate concentration. This concentration will not change in the settling and filtration steps; therefore, the values of b_9 and b_{10} may be set at 0.00010 and 0.00025, respectively. The expression for K_4 may now be expressed as a function of the sulfate concentration of the untreated AMD water, b_3, as follows:

$$K_4 = \frac{0.00015}{(b_3 - 0.00025)}$$

The system may now be solved by inputting the values a_4 , a_5 , a_6 , a_7 , a_8 , a_{10} , a_{11} , a_{12} and b_3 . The "a" values were extracted from the settling and filtration (Section V) analysis sections and are listed below. The value of a_{11} was measured in the laboratory as 0.0005 following carbonation.

Inputting the "a" and "b" concentrations into the "K" equations yields the following numerical values.

$K_1 = 0.31$

$K_2 = 0.19$

$K_3 = 0.01$

$K_4 = 0.31$

The equation for component flow rates, X_i , can now be solved systematically using the calculated "K" values.

X_1 = 200,366 liters per day (52,937 gal/day)

X_2 = 156,252 liters per day (41,282 gal/day)

X_3 = 44,144 liters per day (11,655 gal/day)

X_4 = 156,252 liters per day (41,282 gal/day)

X_5 = 48,437 liters per day (12,797 gal/day)

X_6 = 107,816 liters per day (28,485 gal/day)

X_7 = 9,201 liters per day (2,431 gal/day)

X_8 = 39,235 liters per day (10,366 gal/day)

X_9 = 147,051 liters per day (38,851 gal/day)

X_{10} = 191,165 liters per day (50,506 gal/day)

X_{11} = 1,915 liters per day (506 gal/day)

Product water = 189,250 liters per day (50,000 gal/day)

The quantities of waste solids generated in streams X_7 and X_{11} are calculated below:

$(Solids)_7 = 8.33a_7X_7 = 8.33(0.10)(2,431) = 918$ kg/day (2,025 lb/day)

$(Solids)_{11} = 8.33a_{11}X_{11} = 8.33(0.05)(506) = 96$ kg/day (211 lb/day)

Total solids for disposal = $(Solids)_7 + (Solids)_{11}$ = 1,014 kg/day (2,236 lb/day)

The individual tank capacities necessary for effective performance were determined by calculating the product of the experimental residence time and the hydraulic loading on the tank as determined by the material balances. Residence times have been discussed in the previous analytical sections. These results indicate the residence times for the reactor and carbonator are 90 and 60 min, respectively. Settling tests (Section V, Figure 8) revealed that only 30 min were necessary for efficient separation. The settling time for the demonstration plant has been increased to 60 min to allow for turbulence due to injection and discharge of materials. The feed tank was sized for a residence time of 90 min for flow equalization as well as to minimize fluctuations in pollutant concentrations. A final storage and recarbonation tank was provided for product water storage and pH adjustment, if necessary. An arbitrary 15 min residence time was selected for this tank. Table 16 summarizes residence times, hydraulic loadings, and calculated capacities for each tank.

Table 16. TANK CAPACITIES FOR 190,000 LITER PER DAY (50,000 GAL/DAY) DEMONSTRATION PLANT

Tank	Residence time (days)	Hydraulic loading ℓ/day (gal/day)	Capacity ℓ (gal)
Feed	0.063	200,101 (52,937)	12,606 (3,335)
Reactor	0.063	156,046 (41,232)	9,832 (2,601)
Settler	0.042	156,046 (41,282)	6,517 (1,734)
Carbonator	0.042	191,913 (50,506)	8,017 (2,121)
Final storage	0.010	189,000 (50,000)	1,890 (500)

The sand filters were designed on the basis of experimental results from Section V and solids loading calculations. The solids produced in the reactor and carbonator are similar in their dewatering, or filtering characteristics; therefore, the filtration study conducted on the reactor effluent is applicable to that of the carbonator. The design criterion, which was developed from the experimental study, is the solids filtration capacity, 31 kg/day/m^2 (6.3 lb/day/ft^2). This value is independent of the solids concentration in the feed to the filter, therefore, it is an adequate value for both primary and final filters. When the solids loading rate, $(Solids)_i$, is divided by the solids filtration capacity, the filter area is calculated. The solids loading rates on the primary and final filters were previously calculated as 919 kg/day (2,025 lb/day) and 96 kg/day (211 lb/day), respectively.

Primary filter: Area = 919/31 = 30 m^2 (323 ft^2)

Final filter: Area = 96/31 = 3.1 m^2 (33 ft^2)

The solids represent the "dry weight" of sludge material which is about 50% by weight water of hydration not removed at 105°C. The solids collected on the sand filter are about 10% dry and 90% free water.

Solids collected on the sand filter will be scraped off and disposed of on land. The solids have a density of approximately 1.1 g/cm^3 (70 lb/ft^3), yielding about 9 m^3 (320 ft^3) of sludge per day for disposal.

DEMONSTRATION PLANT EQUIPMENT SELECTION

Preliminary corrosion tests were conducted during the operation of the bench pilot scale AMD plant to assist in selection of materials of construction for the 190,000 liter per day (50,000 gal/day) demonstration plant. The corrosion tests showed that ferrous metals would corrode in contact with the acid mine water and also in the highly alkaline (pH 11.9 to 12.1) reaction mixture. Therefore, plastic materials of construction were chosen for all equipment in contact with the acid and alkaline solutions. Fiberglass was chosen for the storage tank reactor, the settler and carbonator. In addition to corrosion control, product purity was also a determining factor. Corrosion products could have an adverse impact on product water quality.

The bill of materials with costs is given in Table 17. The costs in this table were obtained by written quotations from manufacturers and vendors. The total equipment cost for the 190,000 liter per day (50,000 gal/day) plant is $46,290 with freight estimated at $1,200. A quotation was received for a chlorinator, which may or may not be added later. The chlorinator cost is $2,715.

SCHEDULING AND MANPOWER REQUIREMENTS FOR THE DEMONSTRATION PLANT

The plant construction and installation cost are estimated to be $48,600, which will include all subcontract work such as electrical, concrete and rigging. The sand filters will be constructed on-site and the associated costs are included in those estimated for construction and installation.

The startup of the demonstration plant will require the services of three people for a one-shift, 5-day-week operation; two operators and a supervisor, who will be responsible for the analytical work and data keeping as well as the personnel scheduling.

The continuous operation of the demonstration plant on three shifts, 7 days a week, will require eight operators plus a supervisor.

Table 17. BILL OF MATERIALS FOR DEMONSTRATION PLANT (50,000 GAL/DAY) ACID MINE DRAINAGE TO DRINKING WATER

1 - Raw water 152 ℓpm 30 m (40 gpm 100 ft) head - plastic lined Centrifugal pump with bypass system	$ 1,065
1 - Raw water storage tank 15,000 ℓ (3,950 gal) - fiberglass	2,256
1 - Stage 1 reactor 12,600 ℓ (3,300 gal) dished Bottom tank with baffles - fiberglass	4,215
1 - Turbine blade mixer	2,852
1 - Centrifugal pump - 114 ℓpm 7.5 m (30 gpm 25 ft) head - plastic lined	1,016
1 - Settler 6,500 ℓ (1,690 gal) dished bottom tank - fiberglass	2,384
1 - Centrifugal pump 76 ℓpm 7.5 m (20 gpm 25 ft) head - plastic lined	1,013
1 - Slurry pump - positive displacement 57 ℓpm (15 gpm) - diaphragm	3,142
1 - Sand filter - 18 sq m (200 sq ft) x 0.3 m (1 ft) deep with sludge distributor, repair and recondition present trickle filter	1,000
1 - Centrifugal pump - 57 ℓpm 7.5 m (15 gpm 25 ft) head - plastic lined	1,013
1 - Carbonator 15,850 ℓ (4,170 gal) dished bottom tank with baffles - fiberglass	4,684
1 - Turbine blade mixer	2,852
1 - Centrifugal pump - 152 ℓpm 30 m (40 gpm 100 ft) head open impelier - plastic lined	1,412
1 - Sand filter - 7 sq m (78 sq ft) x 0.3 m (1 ft) deep with distributor	3,500
1 - Centrifugal pump - 152 ℓpm 7.5 m (40 gpm 25 ft) head - plastic lined	1,065
1 - Effluent storage and recarbonation tank - 1,900 ℓ (500 gal) - PVC tank	975
1 - Flowmeter 0-122 ℓpm (0-32 gpm) water 1 - Flowmeter 0-46 ℓpm (0-12 gpm) water 1 - PVC-lime slurry tank complete with mixer, slurry pump, and flowmeter 1 - PVC-sodium aluminate feed tank with mixer, pump and flowmeter 1 - Flowmeter 0-114 ℓpm (0-30 gpm) water 1 - Flowmeter 0-57 ℓpm (0-15 gpm) 1 - Carbon dioxide delivery and mixing system 2 - pH flow-through electrodes 1 - two-pen recorder	11,533
Subtotal	$44,961

Piping and valves

150 m (500 ft) 2.54 cm (1 in.) PVC pipe	195
30 m (100 ft) 1.91 cm (3/4 in.) PVC pipe	30
50 - 2.54 cm (1 in.) L's PVC	16.50
10 - 1.91 cm (3/4 in.) L's PVC	1.90
20 - 2.54 cm (1 in.) T's PVC	8.20
5 - 1.91 cm (3/4 in.) T's PVC	1.05
25 - 2.54 cm (1 in.) ball valves PVC	536.25
10 - 1.91 cm (3/4 in.) ball valves PVC	178.00
10 - 2.54 cm (1 in.) diaphragm valves PVC	255.00
5 - 1.91 cm (3/4 in.) diaphragm valves PVC	107.75
Subtotal	$ 1,319.66
Total	$46,280.66
Freight	$ 1,200
1 - Chlorinator for effluent (possible add on at later date)	$ 2,715

APPENDIX B

ALUMINA-LIME-SODA CHEMICAL REQUIREMENTS FOR RECOVERING WATER FROM ACID MINE DRAINAGE

This appendix presents the derivation of formulae presented in Section VII needed to estimate chemical requirements for sodium aluminate and lime used in Stage I of the alumina-lime-soda process, and for carbon dioxide needed in Stage II. The formula for carbon dioxide dosage includes the procedure for proportioning Stage I effluent and raw acid mine drainage in a blend to produce water with a specific sulfate concentration.

SODIUM ALUMINATE (STAGE I)

The addition of sodium aluminate to acid mine drainage will remove sulfate. Sodium aluminate will be available in two forms. Dry sodium aluminate (Dry-$NaAlO_2$) is now commercially available and contains 43% Al_2O_3 and 30% Na_2O. Calcined sodium aluminate (Cal-$NaAlO_2$) is that produced by firing bauxite and soda ash and contains 53% Al_2O_3 and 39% Na_2O. In addition, iron and alumina in the raw AMD will also remove sulfate. Experimental data indicate that sulfate concentrations can be reduced to 100 mg/liter.

General Equation and Definition of Terms

$$R_{SO_4} - E_{SO_4} = A(NaAlO_2) + B(Fe) + C(Al) \qquad (B\text{-}1)$$

where R_{SO_4} = sulfate concentration of raw water, mg/ℓ

E_{SO_4} = sulfate concentration of Stage I effluent, ≥ 100 mg/ℓ

Dry-$NaAlO_2$ = dry sodium aluminate required, g/ℓ

Cal-$NaAlO_2$ = calcined sodium aluminate required, g/ℓ

Fe = total *in situ* iron concentration of raw water, mg/ℓ

Al = *in situ* aluminum concentration of raw water, mg/ℓ

A, B, and C = coefficients needed to convert concentration into sulfate equivalents

Sulfate Removed by Sodium Aluminate

$$A(NaAlO_2) = A \times (2CaSO_4 \cdot Al_2O_3 \cdot 3CaO) \qquad (B\text{-}2)$$

1 g Dry-$NaAlO_2$ = 430 mg Al_2O_3

1 g Cal-$NaAlO_2$ = 530 mg Al_2O_3

1 mmole Al_2O_3 = 102 mg Al_2O_3

1 mmole Al_2O_3 = 2 mmoles SO_4

1 mmole SO_4 = 96 mg/SO_4

A = coefficient

Calculation of A:

$$A(\text{Dry-}NaAlO_2) = \frac{430}{102} \times 2.0 \times 96 = 809$$

$$A(\text{Cal-}NaAlO_2) = \frac{530}{102} \times 2.0 \times 96 = 998$$

Sulfate Removed by in situ Iron

$$B(Fe) = B \times (CaSO_4 \cdot Fe_2O_3 \cdot 3CaO) \qquad (B\text{-}3)$$

56 mg Fe = 1 mmole Fe

1 mmole Fe = 0.5 mmole SO_4

1 mmole SO_4 = 96 mg SO_4

B = coefficient

Calculation of B:

$$B = \frac{0.5 \times 96}{56} = 0.86$$

Sulfate Removal by in situ Aluminum

$$C(Al) = C \times (CaSO_4 \cdot Al_2O_3 \cdot 3CaO) \qquad (B\text{-}4)$$

27 mg Al = 1 mmole Al

1 mmole Al = 0.5 mmole SO_4

1 mmole SO_4 = 96 mg SO_4

C= coefficient

Calculation of C:

$$C = \frac{0.5 \times 96}{27} = 1.78$$

Equation Solution and Substitution

$$g\ NaAlO_2/\ell = \frac{R_{SO_4} - E_{SO_4} - B(Fe) - C(Al)}{A} \qquad (B\text{-}5)$$

$$g\ Dry\text{-}NaAlO_2/\ell = \frac{R_{SO_4} - E_{SO_4} - 0.86(Fe) - 1.78(Al)}{809} \qquad (B\text{-}6)$$

$$g\ Cal\text{-}NaAlO_2/\ell = \frac{R_{SO_4} - E_{SO_4} - 0.86(Fe) - 1.78(Al)}{998} \qquad (B\text{-}7)$$

LIME (STAGE I)

Addition of lime to raw AMD will (a) neutralize acid, (b) precipitate metals, (c) stabilize sulfoaluminate and sulfoferrite sludge, and (d) maintain process pH at 12.0. In addition, the caustic soda (Na_2O) sodium aluminate provides hydroxide which can substitute for part of the lime. Lime to be used is hydrated lime having 93% purity.

General Equation and Definition of Terms

$$CaO = \sum_{n=a}^{h} CaO_n = A(acid) + B(Mg) + C(Mn) + D(Fe) + E(Al) + (F\text{-}H)(NaAlO_2) + G \qquad (B\text{-}8)$$

where CaO = hydrated lime, 93% $Ca(OH)_2$, requirement, g/ℓ

CaO_n = hydrated lime, 93% CaO, required for specific chemical reaction, g/ℓ

acid = acidity of raw water, mg/ℓ as $CaCO_3$

Mg = magnesium concentration of raw water, mg/ℓ

Mn = manganese concentration of raw water, mg/ℓ

Fe = total iron concentration of raw water, mg/ℓ

Al = alumina concentration of raw water, mg/ℓ

Dry-$NaAlO_2$ = dry sodium aluminate requirement, g/ℓ

Cal-$NaAlO_2$ = calcined sodium aluminate requirement, g/ℓ

A, B, C, D, E, F, and H = coefficients

G = constant to maintain causticity at 600 mg/ℓ (as $CaCO_3$) to maintain process pH at 12.0.

Neutralization

$$CaO_a = A(acid) \qquad (B\text{-}9)$$

1 g lime = 930 mg $Ca(OH)_2$

74 mg $Ca(OH)_2$ = 1 mmole CaO

100 mg acid = 1.0 mmole acid

1.0 mmole acid = 1.0 mmole CaO

Calculation of A:

$$A = \frac{1}{930} \times \frac{74}{100} = 0.00079$$

Precipitation of Magnesium and Manganese

$$CaO_b = B(Mg) \qquad (B\text{-}10)$$

$$CaO_c = C(Mn) \qquad (B\text{-}11)$$

24 mg Mg = 1 mmole Mg

1 mmole Mg = 1 mmole CaO

55 mg Mn = 1 mmole Mn

1 mmole Mn = 1 mmole CaO

1 g CaO = 930 mg $Ca(OH)_2$

1 mmole CaO = 74 mg $Ca(OH)_2$

B, C = coefficients

Calculation of B:

$$B = \frac{1}{930} \times \frac{74}{55} = 0.00332$$

Calculation of C:

$$C = \frac{1}{930} \times \frac{74}{55} = 0.00145$$

Stabilization of Sludge Formed From in situ Iron and Alumina

$$CaO_d = D(Fe) = D \times (CaSO_4 \cdot Fe_2O_3 \cdot 3CaO) \qquad \text{(B-12)}$$

$$CaO_e = E(Al) = E \times (CaSO_4 \cdot Al_2O_3 \cdot 3CaO) \qquad \text{(B-13)}$$

56 mg Fe = 1 mmole Fe

27 mg Al = 1 mmole Al

1 mmole Fe = 1.5 mmole CaO

1 mmole Al = 1.5 mmole CaO

1 mmole CaO = 74 mg $Ca(OH)_2$

1 g lime = 930 mg $Ca(OH)_2$

D, E = coefficients

Calculation of D:

$$D = \frac{1}{930} \times \frac{74}{56} \times 1.5 = 0.00213$$

Calculation of E:

$$E = \frac{1}{930} \times \frac{74}{27} \times 1.5 = 0.00442$$

Stabilization of Sludge Formed From Sodium Aluminate

$$CaO_f = F(NaAlO_2) = F \times (2CaSO_4 \cdot Al_2O_3 \cdot 3CaO) \qquad (B\text{-}14)$$

1 g Dry-$NaAlO_2$ = 430 mg Al_2O_3

1 g Cal-$NaAlO_2$ = 530 mg Al_2O_3

102 mg Al_2O_3 = 1 mmole Al_2O_3

1 mmole Al_2O_3 = 3.0 mmole CaO

1 mmole CaO = 74 mg $Ca(OH)_2$

1 g lime = 930 mg $Ca(OH)_2$

F = coefficient

Calculation of F:

$$F\ (\text{Dry-}NaAlO_2) = \frac{1}{930} \times \frac{74}{102} \times 3.0 \times 430 = 1.006$$

$$F\ (\text{Cal-}NaAlO_2) = \frac{1}{930} \times \frac{74}{102} \times 3.0 \times 530 = 1.240$$

Excess Lime for pH Control

$$CaO_g = G \qquad (B\text{-}15)$$

600 mg/ℓ as $CaCO_3$ causticity = pH 12

600 mg = 6.0 mmole $Ca(OH)_2$

1 g lime = 930 mg $Ca(OH)_2$

74 mg $Ca(OH)_2$ = 1 mmole $Ca(OH)_2$

G = constant

Calculation of G:

$$G = \frac{6.0 \times 74}{930} = 0.477$$

Lime Equivalent From Sodium Aluminate

$$CaO_h = - H(NaAlO_2) \qquad (B\text{-}16)$$

1 g Dry-$NaAlO_2$ = 300 mg Na_2O

1 g Cal-$NaAlO_2$ = 1 mmole Na_2O

1 mmole Na_2O = 1 mmole CaO

1 g lime = 930 mg $Ca(OH)_2$

1 mmole CaO = 74 mg $Ca(OH)_2$

H = coefficient

Calculation of H:

$$H\ (\text{Dry-}NaAlO_2) = \frac{1}{930} \times \frac{74}{62} \times 300 = 0.385$$

$$H\ (\text{Cal-}NaAlO_2) = \frac{1}{930} \times \frac{74}{62} \times 390 = 0.501$$

Summation and Combination

$$g\ CaO/\ell = \sum_{n=a}^{h} CaO_n = A(acid) + B(Mg) + C(Mn) + D(Fe) + E(Al) + G + (F-H)NaAlO_2 \qquad (B\text{-}17)$$

$$g\ CaO/\ell\ (\text{Dry-}NaAlO_2) = [0.00079\ acid + 0.00332\ Mg + 0.00145\ Mn + 0.00213\ Fe + 0.00442\ Al + 0.477] + 0.621\ g\ \text{Dry-}NaAlO_2 \qquad (B\text{-}18)$$

$$g\ CaO/\ell\ (\text{Cal-}NaAlO_2) = [0.00079\ acid + 0.00332\ Mg + 0.00145\ Mn + 0.00213\ Fe + 0.00442\ Al + 0.477] + 0.739\ g\ \text{Cal-}NaAlO_2 \qquad (B\text{-}19)$$

CARBON DIOXIDE (STAGE II)

Effluent from Stage I of the alumina-lime-soda process contains 600 mg/liter (as $CaCO_3$) of causticity and must be neutralized. In addition, the effluent will have a sulfate level of about 100 mg/liter. This effluent can be blended with raw AMD to bring the sulfate level in product water to 250 mg/liter, the maximum permissible level for drinking water. This blending procedure reduces the carbon dioxide requirements for complete neutralization.

Carbon dioxide is added to drop pH to 10.3 and also precipitates the maximum amount of $CaCO_3$; the carbonate concentration at pH 10.3 will be about 35 mg/liter as $CaCO_3$. After separating the $CaCO_3$ from the product water, it is carbonated further to reduce pH to the 7.0 to 8.0 range. The 35 mg/liter carbonate will be converted to 35 mg/liter bicarbonate. The conversion of carbonate to bicarbonate will require additional carbon dioxide.

Fraction of Stage I Effluent in Blend with Raw AMD

$$\frac{R_{SO_4} - P_{SO_4}}{R_{SO_4} - E_{SO_4}} = EFF \qquad (B\text{-}20)$$

where EFF = fraction of Stage I effluent in the blend

R_{SO_4} = sulfate concentration of raw AMD, mg/ℓ

E_{SO_4} = sulfate concentration of Stage I effluent, ≥ 100 mg/ℓ

P_{SO_4} = sulfate concentration of product water, ≥ 250 mg/ℓ

thus,
$$1 - EFF = AMD \qquad (B\text{-}21)$$

where AMD = fraction of raw AMD in the blend

Causticity of Blend

$$(EFF \times 600) - (AMD \times acid) = CAUS \qquad (B\text{-}22)$$

where CAUS = causticity of blend, in mg/ℓ as $CaCO_3$

Carbon Dioxide

$$CO_2 = A \times (CAUS + 35) \qquad (B\text{-}23)$$

where CO_2 = carbon dioxide requirement, g/ℓ

1 mmole
causticity = 100 mg as $CaCO_3$

1 mmole
causticity = 1 mmole CO_2

35 mg
carbonate = 35 mg bicarbonate = 35 mg as $CaCO_3$

44 mg CO_2 = 1 mmole CO_2

1 mg CO_2 = 0.001 g CO_2

carbonation
efficiency = 0.95

A = coefficient

Calculation of A:

$$A = \frac{44}{100} \times \frac{1}{0.95} \times 0.001 = 0.00046$$

Substitution Into CO_2 Requirement Equation

$$g\ CO_2/\ell = 0.00046 \times (CAUS + 35) \qquad (B\text{-}24)$$

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